

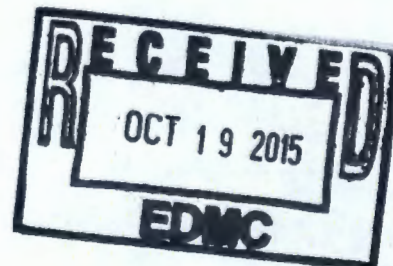
Performance Report for the 2011 Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788



P.O. Box 1600
Richland, Washington 99352



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Release Approval

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Executive Summary

The apatite permeable reactive barrier (PRB) is designed to reduce the flux of strontium-90 from the groundwater along the 100-N Area shoreline to the Columbia River. During 2011, the apatite barrier was extended from 91 m (300 ft) to 274 m (900 ft) by injections of apatite-forming solutions through wells into the aquifer. This report on the 2011 injections of apatite-forming solutions describes the apatite sequestration technology, the operations and solution delivery design and equipment used, as well as the sampling and analyses conducted in support of the injections. The data collected during and following the injections are included in this report and are used to evaluate the optimization methods tested.

Background

During 2006 through 2008, a treatability test was conducted in the 100-N Area to evaluate the effectiveness of an apatite PRB for removing strontium-90 from groundwater. During the treatability test, apatite-forming solutions were injected into 16 wells to form a 91 m (300 ft) long apatite barrier parallel to the river. The solutions contained calcium, citrate, and phosphate where the presence of citrate prevented immediate precipitation of calcium and phosphate. After the solutions were injected, biodegradation of the citrate released the calcium and resulted in the precipitation of apatite, a calcium phosphate mineral, within the aquifer. Apatite sequesters strontium ions in groundwater by cation exchange and through substitution for calcium ions in the apatite structure where the strontium is immobilized and radioactively decays over time. The apatite PRB is designed to sequester strontium for approximately 300 years and mitigate movement of strontium-90 toward the river. During this time period, strontium-90 in the plume and barrier will radioactively decay to below the drinking water standard (DWS). Based on the results of laboratory testing and the field-scale treatability testing, the treatability test report (PNNL-19572¹) included recommendations for the apatite-forming injection solution formulation, target injection volumes, and injection timing, relative to river level, for shallow and deep aquifer zones.

¹ PNNL-19572, 2010, *100-NR-2 Apatite Treatability Test: High-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization Final Report*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-19572.pdf.

Based on the success of the treatability test, the interim action record of decision (ROD) was amended (EPA, 2010²) to select apatite sequestration as the remedy for strontium-90 along the river shoreline. The amended ROD (EPA, 2010) specified that (1) the apatite barrier be extended from 91 m (300 ft) to approximately 762 m (2,500 ft); and (2) the barrier initially be extended 91 m (300 ft) to the southwest (upriver) and 91 m (300 ft) to the northeast (downriver) to optimize the injection well design and apatite solution composition prior to full-scale deployment.

In 2009 and 2010, 146 injection wells were installed to create the 762 m (2,500 ft) long apatite barrier injection well network. The wells are alternately screened in a shallower aquifer zone (3.0 to 4.6 m [10 to 15 ft] below ground surface [bgs]) and a deeper aquifer zone (5.2 to 7.3 m [17 to 24 ft] bgs) within the interval of highest detectable sediment and groundwater contamination. Twenty-five performance monitoring wells, all screened in the deeper aquifer zone, were installed downgradient of the barrier injection network (between the network and the river). Pre-injection groundwater samples were collected from all injection and performance wells in 2010.

2011 Implementation

In 2011, apatite-forming solutions were injected into 24 wells in the 91 m (300 ft) long segment southwest (upriver) of the original (treatability test) barrier and into 24 wells in the 91 m (300 ft) long segment northeast (downriver) of the original barrier.

The injections were conducted as a design optimization study to evaluate approaches for moving from the scale of the treatability test to the larger scale of complete barrier deployment. These first large-scale injections in 2011 tested operational and apatite solution delivery options.

The apatite-forming solutions injected in 2011 were the same formulation as recommended in the treatability test report. Two injection skids, designed and built for blending the apatite-forming solutions with river water at controlled ratios and flow rates and injecting the mixed solution into as many as 6 injection wells simultaneously, were used for the 2011 injections.

² EPA, 2010, *U.S. Department of Energy 100-NR-1 and NR-2 Operable Units Hanford Site – 100 Area Benton Country, Washington Amended Record of Decision, Decision Summary and Responsiveness Summary*, U.S. Environmental Protection Agency, Seattle, Washington. Available at: <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0084198>.

All of the injections were conducted in September 2011, during relatively low river levels, in four phases. All 12 of the upriver deep wells were injected simultaneously (i.e., every other upriver well) using the two skids, followed by all 12 of the upriver shallow wells. All 12 of the downriver deep wells then were injected simultaneously, followed by all 12 of the downriver shallow wells. During each phase, injection operations continued 24 hours/day until all of the planned solution volume had been injected.

Flow meters on the injection skids were designed to keep track of the total volume of solution injected into each well. Samples of the injection solution and river water were collected during the injection periods for laboratory analyses. On-site personnel recorded injection parameters (e.g., flow rates of apatite-forming solutions and river water for blending on the skids). In situ probes installed in selected downgradient performance monitoring wells recorded field parameters (e.g., water levels and specific conductivity).

Three rounds of post-injection samples were collected from the downgradient performance monitoring wells and aquifer tubes in the five weeks following injections to track temporary increases in cations and metals caused by injections of apatite-forming solutions. Subsequently, post-injection samples were collected from the downgradient performance monitoring wells twice in 2012 and twice in 2013, sampling at both high and low river levels each year.

Results

The skids successfully blended the chemical solutions at the prescribed ratios and injected the solutions to six wells simultaneously. However, because of subsurface heterogeneities, the volume of solution injected into each well varied significantly. The screened intervals of the shallow injection wells were unsaturated or partially saturated during the injections at low river levels, limiting the emplacement of apatite in that zone. Injecting adjacent wells simultaneously prevented monitoring within the barrier for the lateral distribution of the apatite-forming solution between wells and likely caused hydraulic interferences from mounding that reduced the lateral coverage between wells. Post-injection monitoring confirmed that the temporary increases in groundwater concentrations of cations and metals resulting from the injection solutions reverted to background concentrations within a few weeks to months following the injections. Monitoring in fall 2013, two years after the 2011 injections, indicates that the

strontium-90 concentrations have been reduced by 71 to 98 percent in seven of the eight downgradient performance monitoring wells. In the eighth well, the pre-injection and fall 2013 concentrations of strontium-90 were below the DWS.

The design optimization testing conducted in 2011 did not result in any significant changes to the recommendations made in the 2010 treatability test report (PNNL-19572). Some of the optimization methods tried could impact the performance of the barrier over time. However, continued performance monitoring will help resolve potential deficiencies that would need to be addressed through, for instance, additional injections.

Recommendations

The following actions are recommended for future injections:

- Inject into the shallow aquifer wells during high river stage. Inject into the deeper aquifer wells at low river stage. Minimize injection of apatite-forming solution into wells with partially unsaturated screened intervals.
- Design the sequence of injection wells to allow monitoring of injection solution distribution laterally between the barrier injection wells during injections.
- Design the sequence of injection wells to minimize hydraulic interference of injected solution volumes and maximize the lateral distribution of the injection solutions.
- During injection operations, discontinue or reduce injections in wells that have received the target injection volume, after monitoring indicates adequate lateral distribution of solution, and continue injecting remaining wells until the target volume has been injected.
- During post-injection monitoring, consider monitoring for gross beta (a less expensive surrogate for strontium-90) in injection wells to increase the spatial resolution of the data.
- Continue to collect performance monitoring data at downgradient monitoring wells to evaluate the apatite emplacement and its long term ability to reduce strontium-90 concentrations reaching the river.

- Conduct pre-injection monitoring in and downgradient of untreated segments of the barrier network at multiple river stages to establish minimum and maximum pre-injection concentrations.
- Evaluate the need for additional performance monitoring wells screened over a longer interval that includes shallower zones.

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Terms

AFD	adjustable frequency drive
amsl	above mean sea level
bgs	below ground surface
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act of 1980</i>
DOE	U.S. Department of Energy
DOS	design optimization study
dpm	disintegrations per minute
DWS	drinking water standard
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FIT	flow indicating transmitter
FQI	flow indicating totalizer
FS	feasibility study
ITRD	Innovative Treatment & Remediation Demonstration
NTU	nephelometric turbidity unit
OU	operable unit
PRB	permeable reactive barrier
PVC	polyvinyl chloride
RAO	remedial action objective
RI	remedial investigation
ROD	record of decision
RUM	Ringold Formation Upper Mud
TPH	total petroleum hydrocarbon
TTP	treatability test plan

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1 Introduction

This document presents the results of the design optimization study (DOS) for extension of the apatite permeable reactive barrier (PRB) conducted during 2011 in the 100-NR-2 Operable Unit (OU) (DOE/RL-2010-29, *Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit*). The 100-NR-2 OU is the groundwater underlying the 100-N Area on the Hanford Site (Figure 1-1). The apatite PRB is designed to reduce the flux of strontium-90 from groundwater to the Columbia River. The DOS described the test methods developed to evaluate potentially improved methods for the delivery and emplacement of apatite-forming minerals in the saturated zone.

The DOS was performed under EPA/ROD/R10-99/112, *Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units, Hanford Site, Benton County, Washington*, to fulfill the interim remedial action objective (RAO) of evaluating treatment technologies.

1.1 Background

Operations at 100-N began in 1964 following construction of the 105-N Reactor, the last of the nine Hanford Site plutonium production reactors constructed along the Columbia River between 1943 and 1964. Operation of the 105-N Reactor and associated facilities generated radioactive liquid wastes. The primary liquid waste disposal facilities were the 116-N-1 crib and trench and the 116-N-3 crib and trench (Figure 1-2). Waste site 116-N-1 was constructed approximately 244 m (800 ft) inland from the river. When strontium-90 was detected at the shoreline in nearby wells and river bank seeps, replacement waste site 116-N-3 was constructed further inland.

Irradiated fuel was discharged from the 105-N Reactor to the spent fuel basin and stored in the water-filled basin for about 180 days to allow radioactive decay of short-lived fission products before transfer for reprocessing. The fission products from ruptured irradiated fuel were purged from the fuel storage basin to the 116-N-1 crib and trench from 1963 to 1985 and to the 116-N-3 crib and trench from 1983 to 1991. Essentially, all of the strontium-90 that was discharged to the 116-N-1 and 116-N-3 cribs and trenches was from the fuel storage basin cooling and purge water.

Strontium-90 released from the 116-N-1 and 116-N-3 waste sites contaminated the underlying deep vadose zone and groundwater, which discharged to the Columbia River. Following extensive study and laboratory testing, a treatability test of an apatite PRB began in 2006 with the injection of apatite-forming chemicals into the aquifer through vertical wells along the bank of the Columbia River (DOE/RL-2005-96, *Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit*). The test area, approximately 91 m (300 ft) long, encompassed the highest strontium-90 concentrations observed at the shoreline (Figure 1-3). Based on the treatability testing, the makeup of the apatite-forming chemicals was optimized. The treatability test was successfully concluded in 2009 (PNNL-19572, *100-NR-2 Apatite Treatability Test: High-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization Final Report*).

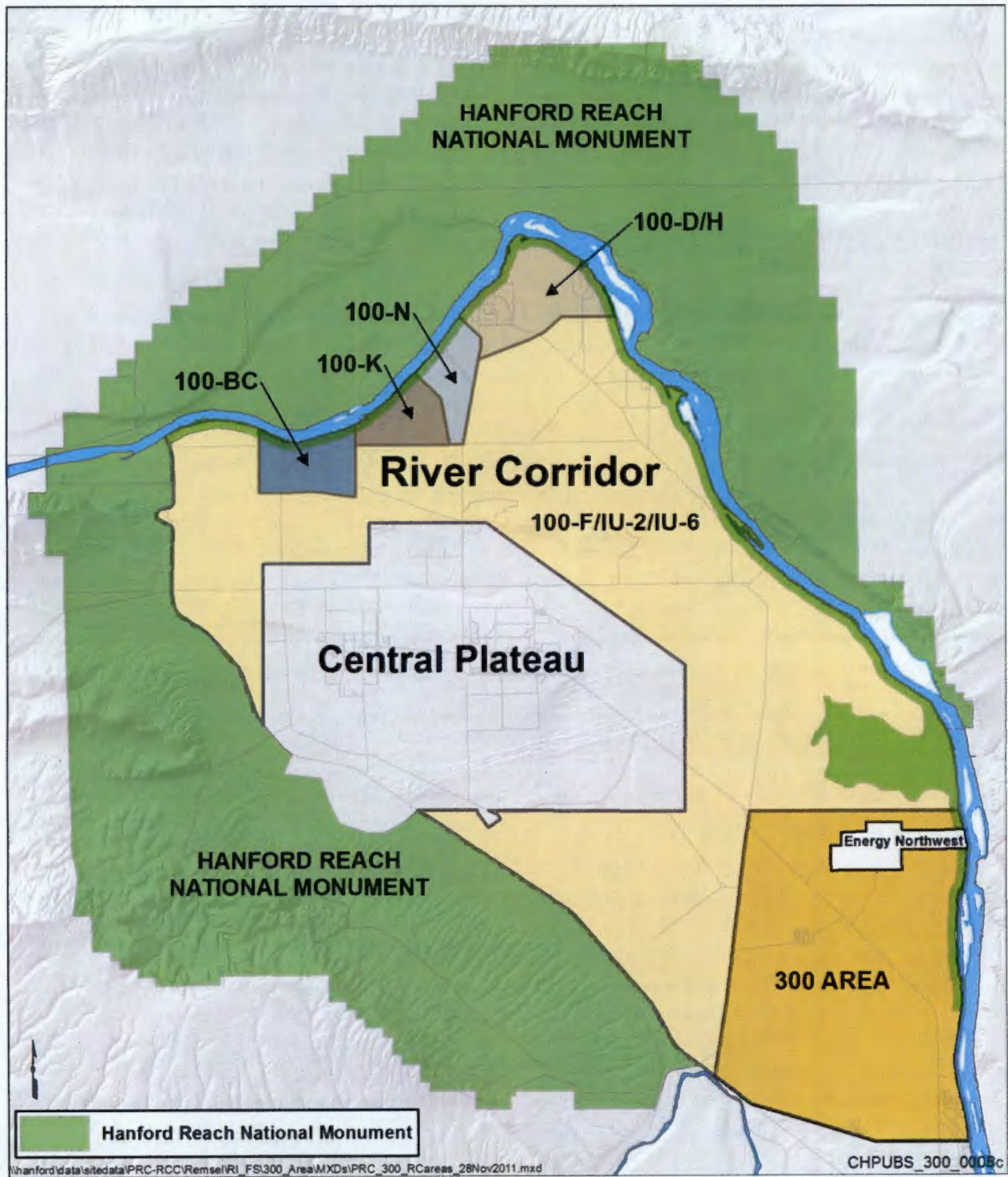


Figure 1-1. Location of 100-N on the Hanford Site



Figure 1-2. Location of Source Waste Sites 116-N-1 (1963-1985) and 116-N-3 (1983-1991)

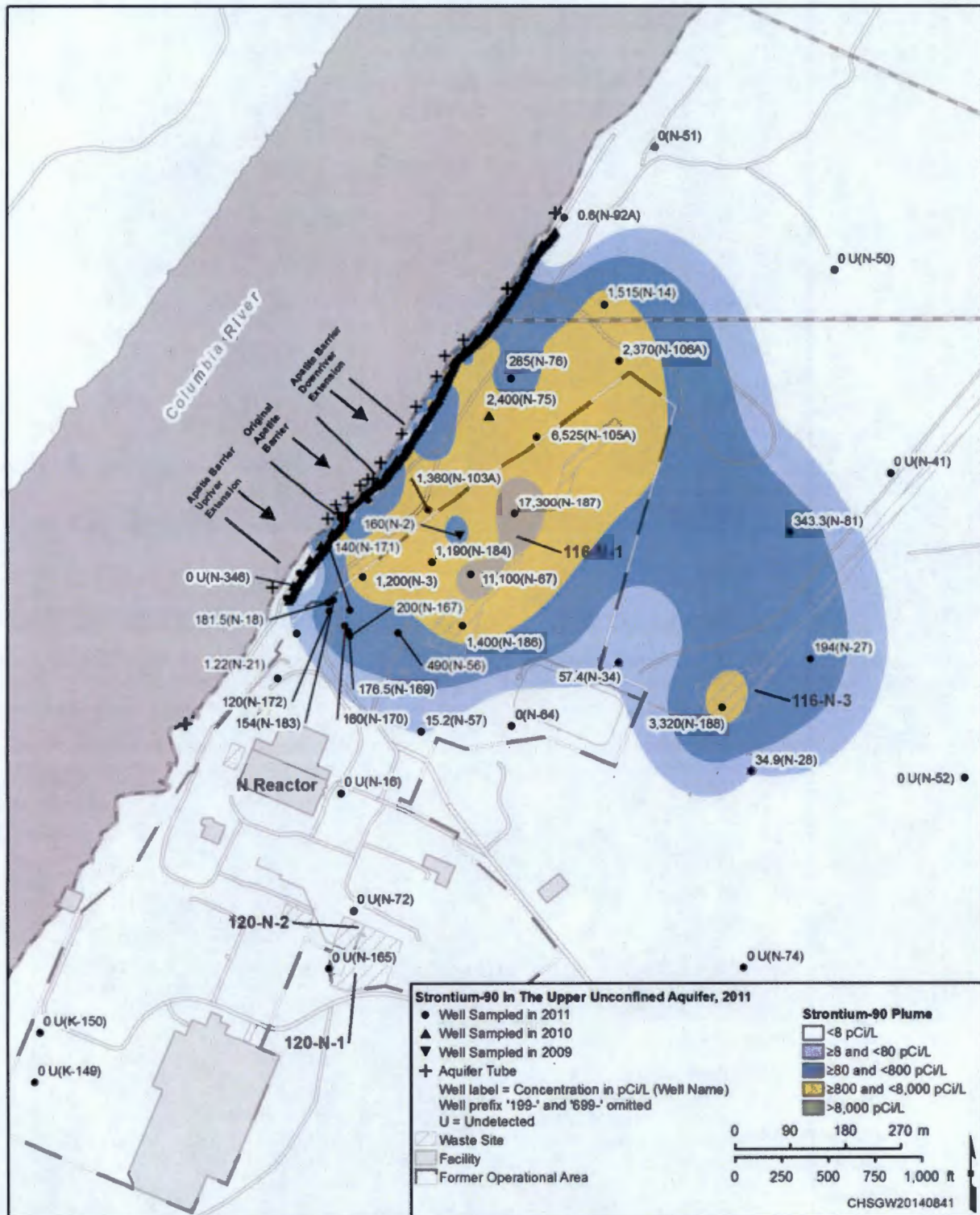


Figure 1-3. Location of the Strontium-90 Plume Concentrations and the Apatite Permeable Reactive Barrier in 2011

Strontium-90 sequestration using this technology occurs by injecting a calcium-citrate-phosphate solution into the aquifer. After the solution is injected, biodegradation of the citrate releases the calcium and results in the precipitation of apatite (a calcium phosphate mineral $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$). Strontium-90 (and strontium) ions in groundwater substitute for calcium ions through cation exchange and eventually become trapped as part of the mineral matrix during apatite crystallization. The apatite PRB is designed to sequester the strontium-90 for approximately 300 years, during which time the immobilized strontium-90 will radioactively decay, through 10 half-lives of 29.1 years each, to below the drinking water standard (DWS).

In 2010, strontium-90 concentrations in groundwater exceeded the DWS (8 pCi/L) along 762 m (2,500 ft) of the 100-N shoreline. Injection wells were installed to allow the apatite PRB to be extended (Figure 1-4). The extension provided the injection wells for future apatite treatment to sequester the strontium-90 detected in groundwater along this section of the Columbia River.

Apatite-forming solutions were injected into the wells in two 91 m (300 ft) long segments of the apatite PRB in 2011. One segment was adjacent to the upriver end of the original treatability test barrier, and one segment was adjacent to the downriver end of the original treatability test barrier (Figure 1-3). The wells were injected as part of the DOS for barrier extension (DOE/RL-2010-29). This report provides results of the 2011 injections.

1.2 Site Description

This section summarizes 100-N hydrogeology and the previous remedial actions and regulatory decisions associated with the 100-NR-2 OU.

1.2.1 Site Location

The Hanford Site is located in southeastern Washington State near Richland, Washington. The 100-N Area of Hanford is one of six geographic areas that border the Columbia River (Figure 1-1). These six geographic areas along the Columbia River are together referred to as the River Corridor. The 100 Area of Hanford is split into five smaller geographic areas (100-BC, 100-K, 100-N, 100-D/H, and 100-F) that include nine nuclear reactors previously used for plutonium production. The 100-NR-2 OU is located in the northern part of the Hanford Site adjacent to the Columbia River.

1.2.2 Site Hydrogeology

Stratigraphic units of significance in 100-N include the Ringold Formation and the Hanford formation (Figure 1-5). The unconfined aquifer at 100-N near the shoreline is composed of gravels and sands of the Ringold Formation and Hanford formation. The Ringold Formation is composed of several lithologic facies; the geologic units most significant to contaminant movement in groundwater at 100-N are the Ringold Formation Unit E (Ringold Unit E), which primarily forms the unconfined aquifer beneath the Hanford formation, and the underlying Ringold Formation Upper Mud (RUM). The base of the unconfined aquifer is defined by the top of the RUM, which is considered an aquitard rather than an impermeable unit.

The uppermost Ringold unit at 100-N is Ringold Unit E, consisting of variably cemented pebble to cobble gravel with a fine- to coarse-grained sand matrix. Sand and silt interbeds also may be present. Ringold Unit E is approximately 12 to 15 m (39 to 49 ft) thick. The underlying RUM is a much less transmissive, relatively thick silty to clayey unit ranging up to 60 m (197 ft) thick.

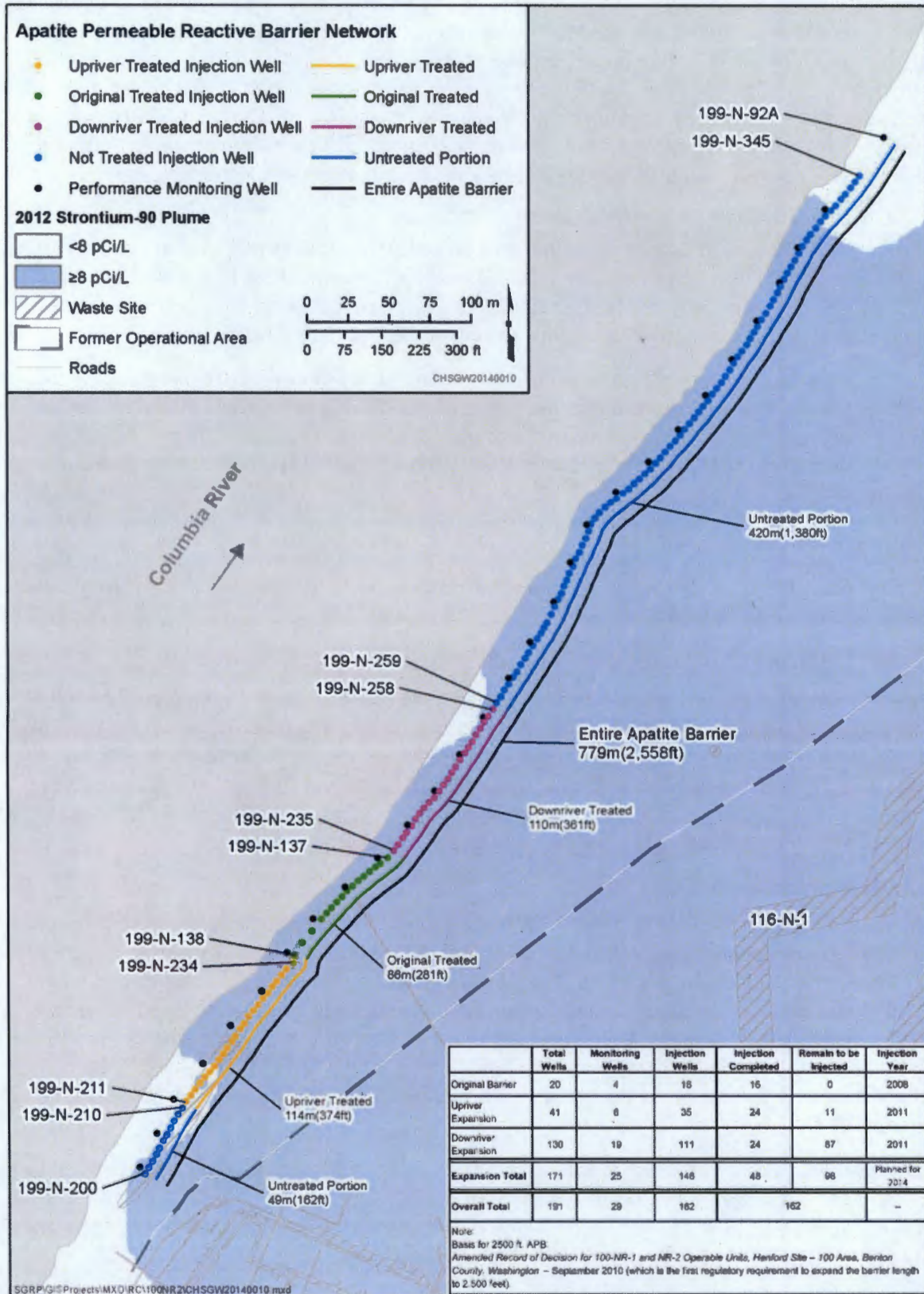


Figure 1-4. Location and Status of Injection Wells in the Apatite Permeable Reactive Barrier

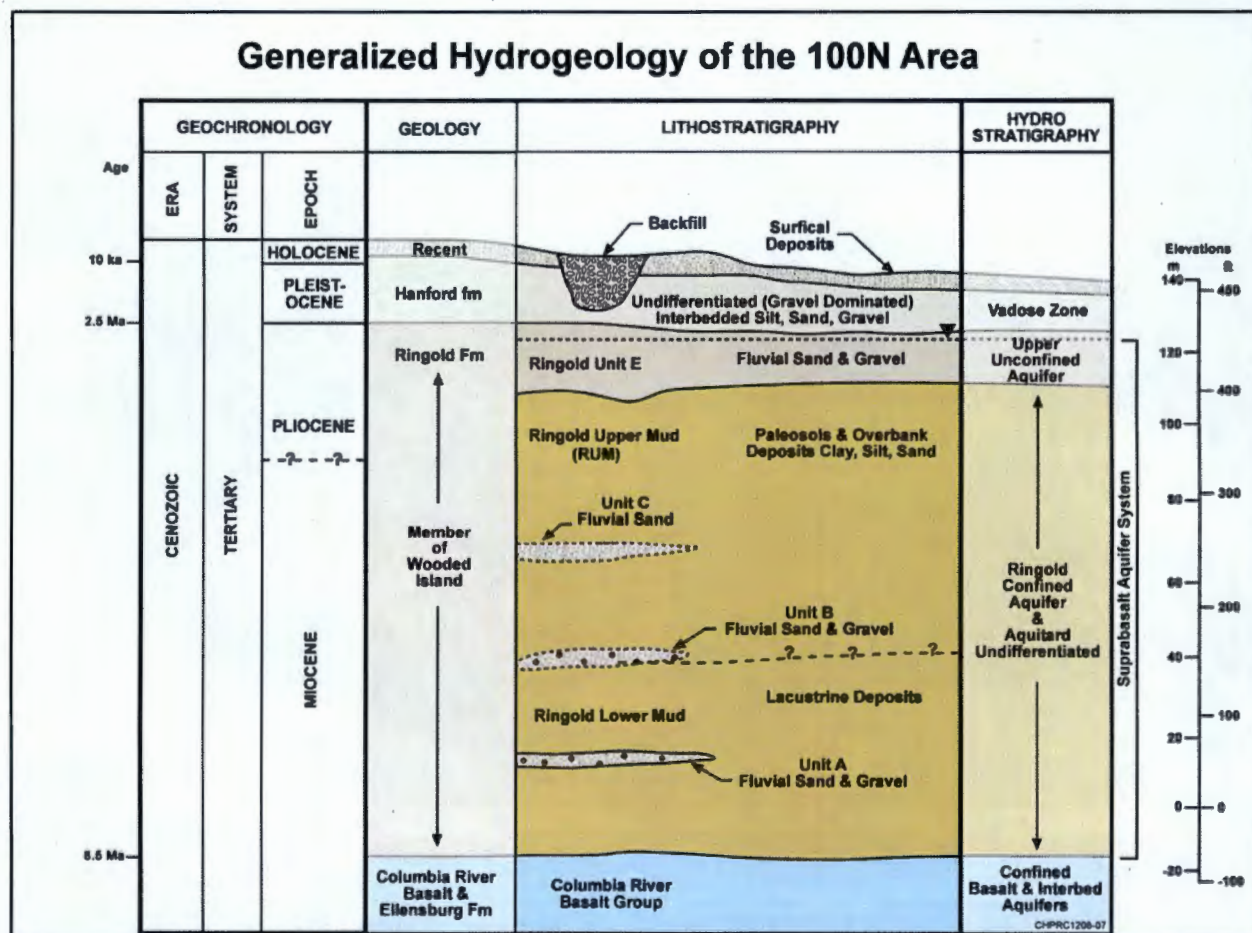


Figure 1-5. Generalized Geologic Stratigraphic Section of 100-N

The uppermost stratigraphic unit in 100-N is the Hanford formation, which consists of uncemented and clast-supported pebble, cobble, and boulder gravel with minor sand and silt interbeds. The matrix in the gravel is composed mostly of coarse-grained sand, and an open-framework texture is common. In most of 100-N, the Hanford formation extends from ground surface to just above the water table, ranging in thickness from 5.8 to 24.5 m (19 to 77 ft). However, paleo-erosional channels filled with Hanford gravels extend below the water table in limited areas at 100-N, mostly near the Columbia River. Figure 1-6 depicts a 3-dimensional cross section of the Hanford and Ringold Unit E in the near-river environment. As illustrated in Figure 1-6, the aquifer extends into the Columbia River channel and the high river stage can rise into the Hanford formation along the river's edge.

The Hanford formation is typically more transmissive (3 to 10 times) than the underlying Ringold Unit E. However, due to geologic heterogeneity, the hydraulic conductivity in both units can be highly variable. Saturated horizontal hydraulic conductivity values of 63.4 and 6.2 m/day (208.0 and 20.3 ft/day) were used as input parameters in numerical simulations for the Hanford formation and Ringold Formation, respectively (Table 5-9 in DOE/RL-2012-15, *Remedial Investigation/Feasibility Study for the 100-NR-1 and 100-NR-2 Operable Units*).

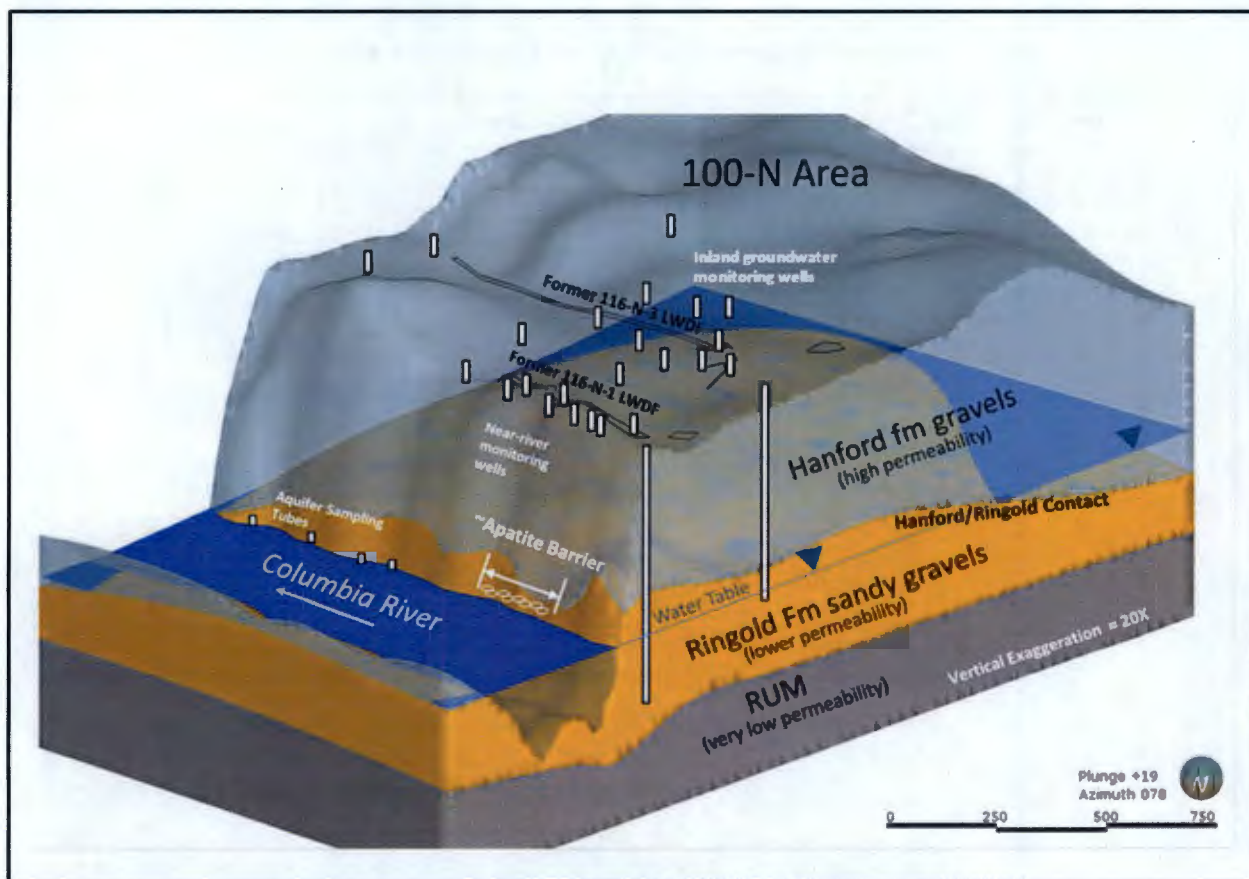


Figure 1-6. 100-N Area Three-Dimensional Hydrogeology Block Diagram

Site-specific hydrogeologic characterization data were gathered during the installation of injection and performance monitoring wells for the apatite PRB treatability test. During the treatability test, two pilot test sites located at the upriver and downriver ends of the original 91 m (300 ft) long barrier segment were used for the initial injections to develop the injection design for the remaining portions of the barrier (Section 1.2.3 of this document). Comparison of test results from these two locations indicate that the permeability contrast between the Hanford formation and Ringold Formation is significantly less over the upriver one-third of this part of the barrier. The estimated horizontal hydraulic conductivity for the Hanford formation and Ringold Formation over the upriver portion of the original barrier is 12 and 10 m/day (39 and 33 ft/day), respectively (Section 6.3 of PNNL-17429, *Interim Report: 100-NR-2 Apatite Treatability Test: Low-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization*). By contrast, the estimated horizontal hydraulic conductivity for the Hanford formation and Ringold Formation over the downriver portion of the original barrier is 29 and 9 m/day (95 and 30 ft/day), respectively.

A detailed hydrogeologic cross section along the entire 762 m (2,500 ft) long apatite barrier well network has been constructed based on geologic characterization data available from drilling and installation of 171 injection and performance monitoring wells completed during the barrier expansion (SGW-47791, *Borehole Summary for the Installation of One Hundred and Seventy One Wells at 100-NR-2 Operable Unit, FY 2009-2010*), and information from the 16 original barrier wells. The cross section is shown in seven segments in Figure 1-7, from southwest (upriver) (Figure 1-7a) to northeast (downriver) (Figure 1-7g). Each segment shows the location of the wells in the network relative to the shoreline; the Hanford-Ringold contacts in the wells; the vertical extent of detected radiological contamination

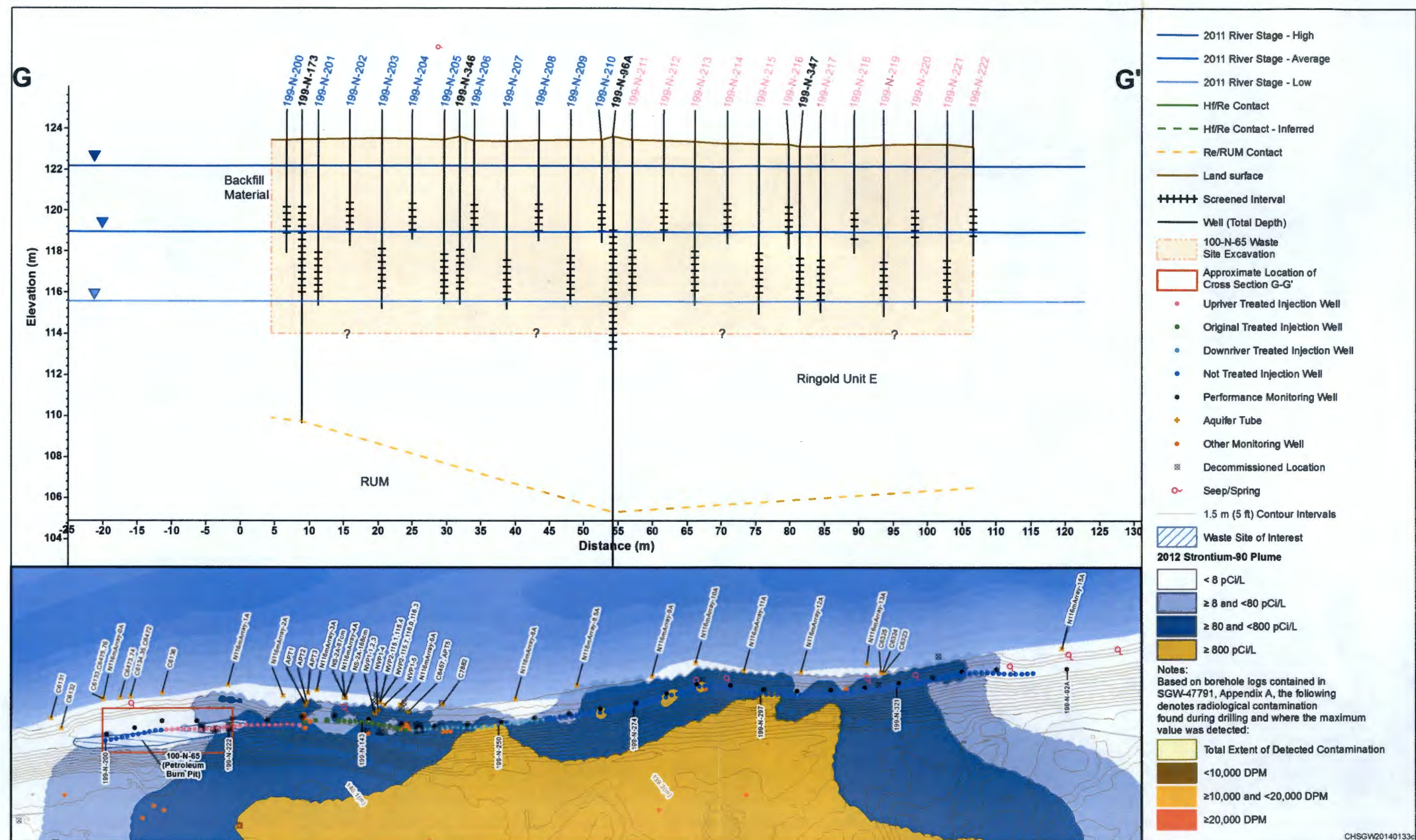


Figure 1-7a. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Southernmost Segment G-G'

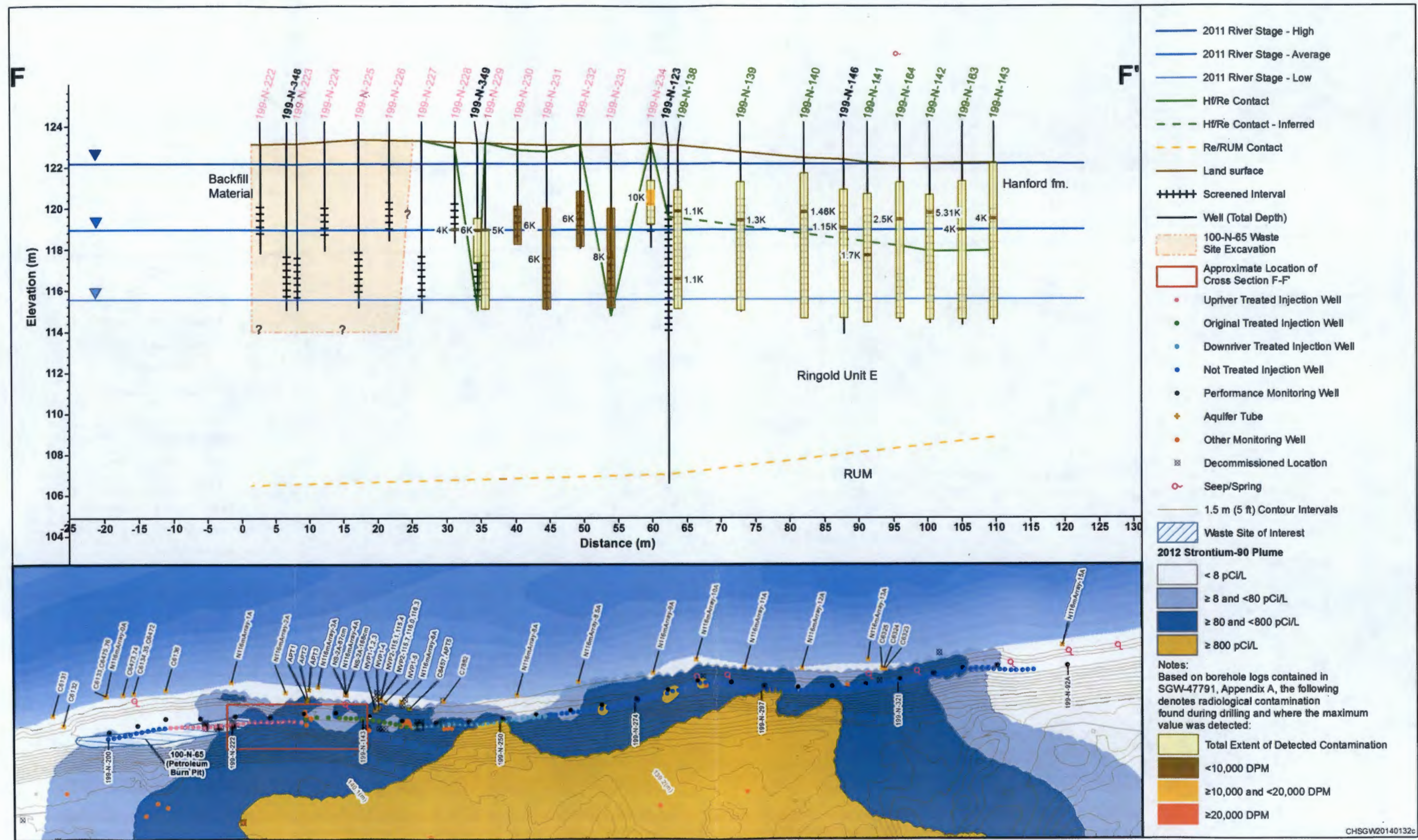


Figure 1-7b. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Segment F-F'

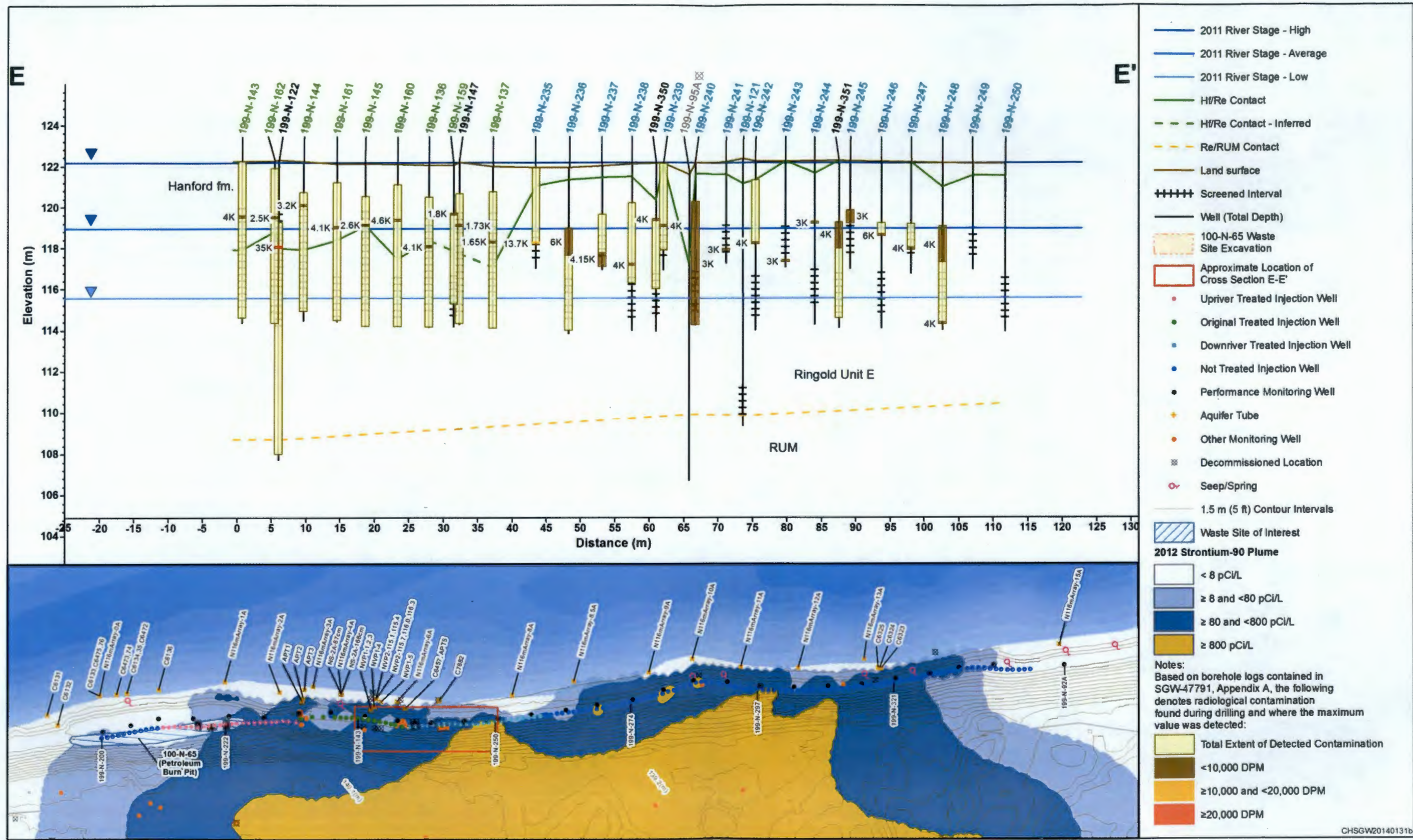


Figure 1-7c. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Segment E-E'

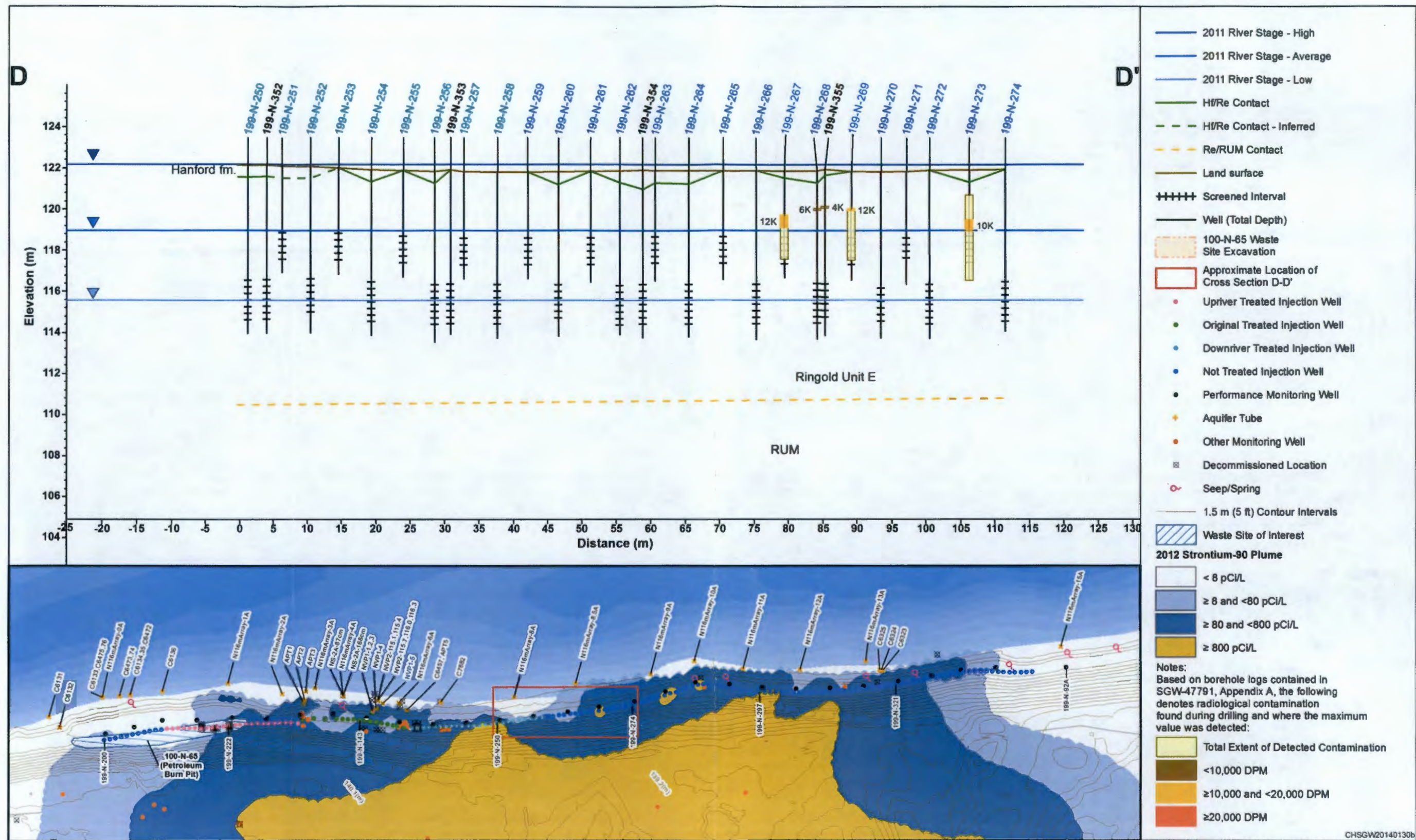


Figure 1-7d. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Segment D-D'

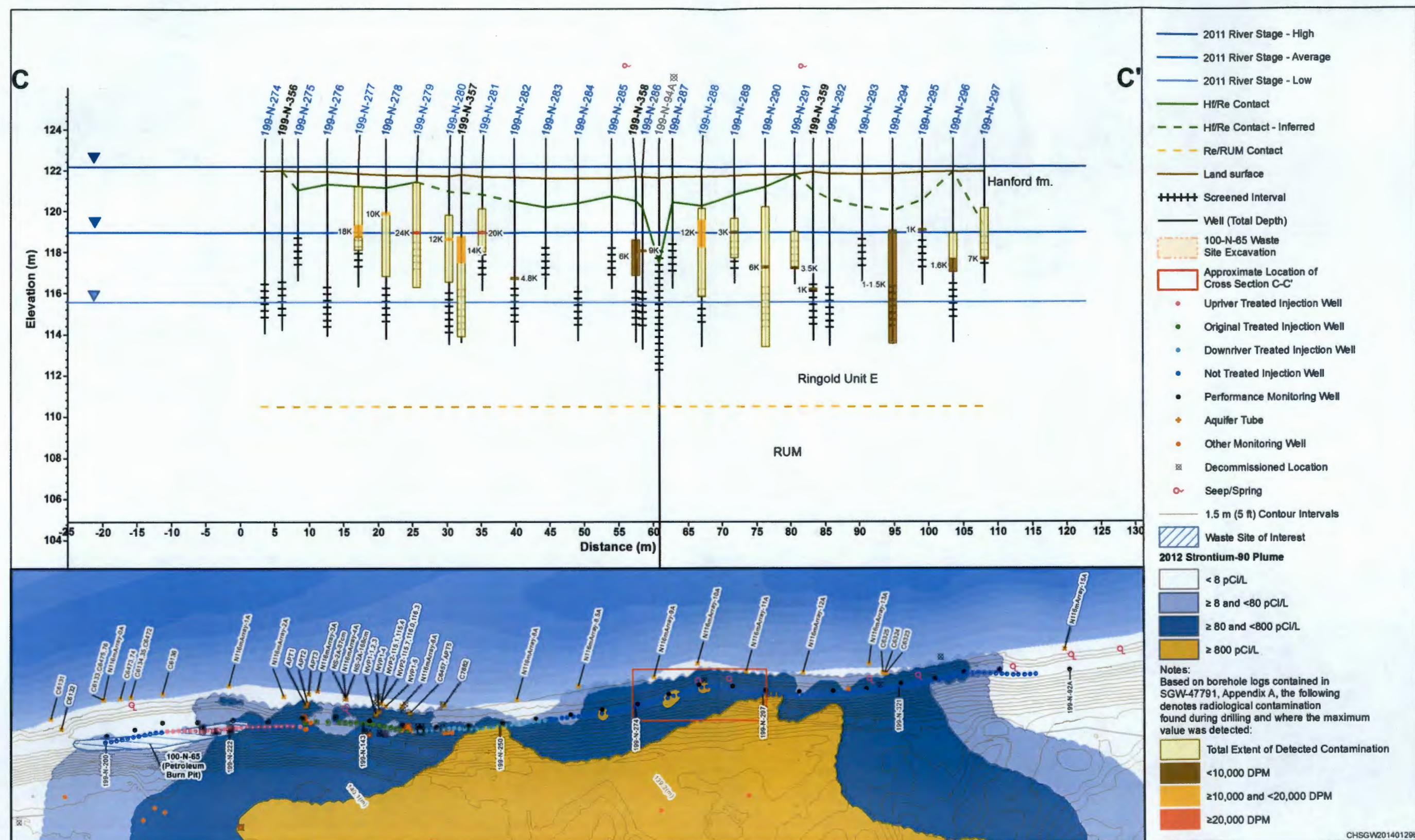


Figure 1-7e. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Segment C-C'

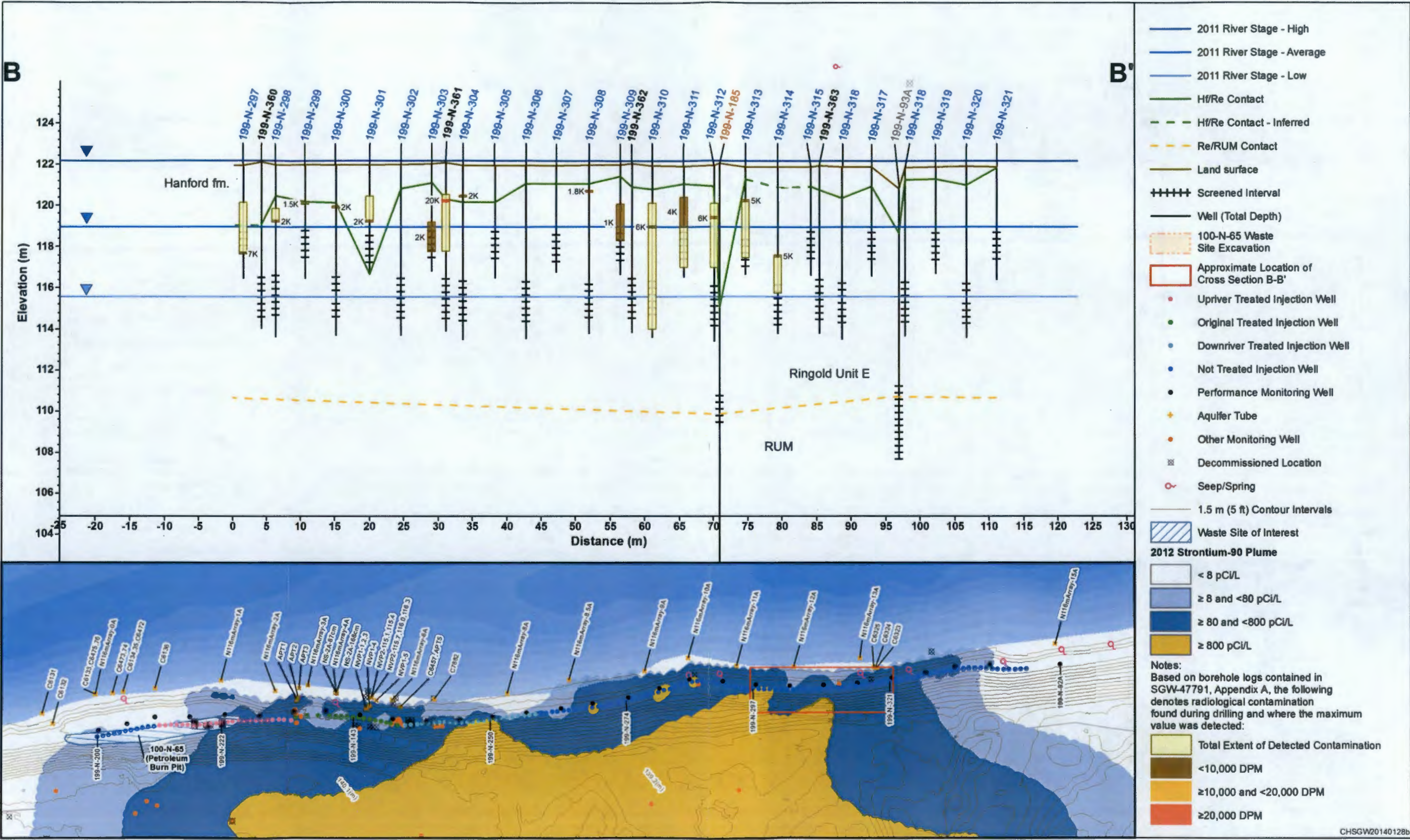
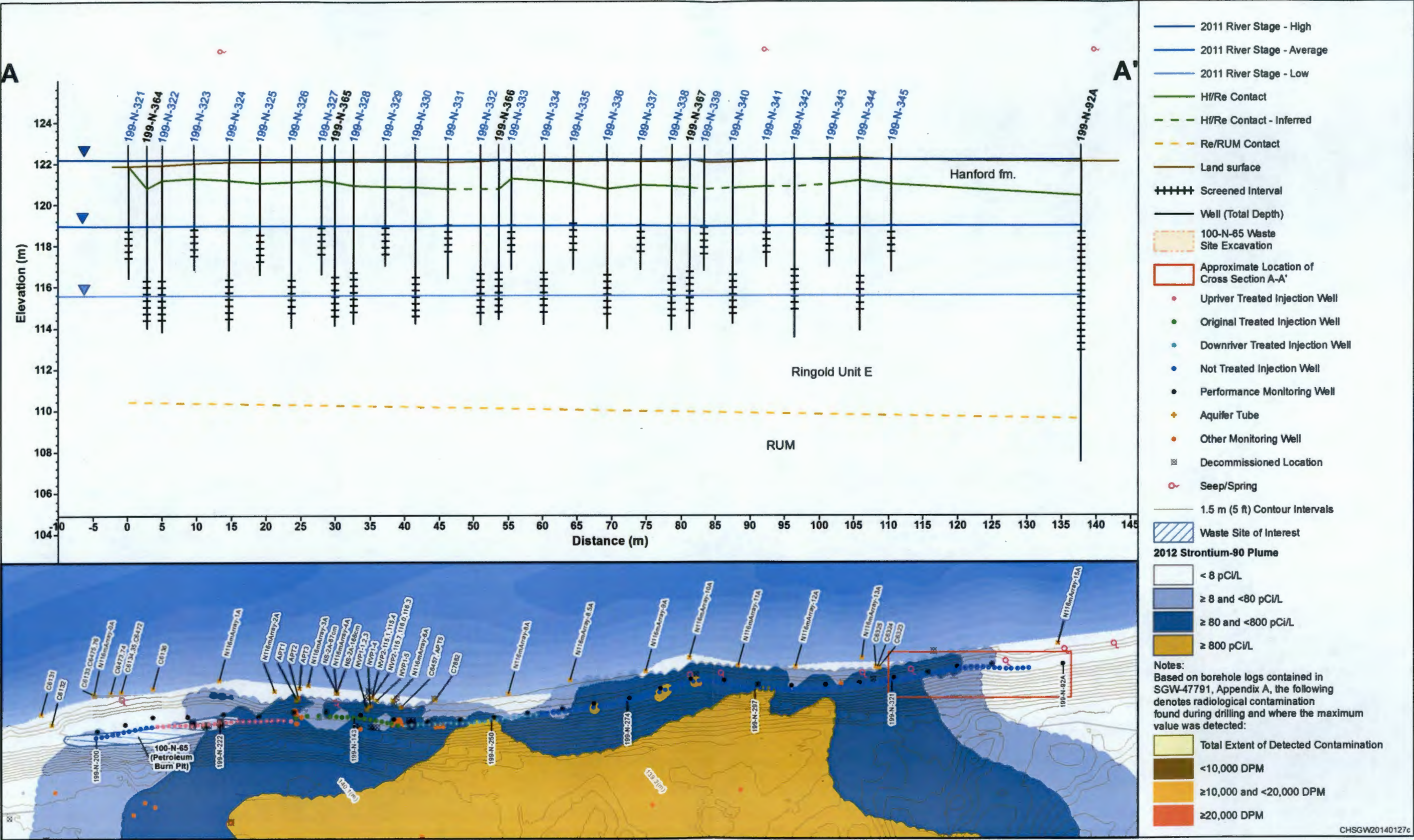


Figure 1-7f. Hydrogeologic Cross Section along the Apatite Permeable Reactive Barrier Well Network, Segment B-B'



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encountered in each borehole during drilling; the 2011 river stage range; the screened intervals in each well; the strontium-90 concentrations in the groundwater plume along the shoreline; the location of the shoreline seep sites detected during past practice operations; and the position of the segment within the entire cross section.

The radiological contamination detected during drilling is depicted by location and vertical extent on the individual borehole profiles along the entire PRB well network. The detected contamination varies from well to well but generally defines a vertical region that extends a few meters above and below the average ambient water table (approximately 119 m above mean sea level [amsl] in 2011); in a few wells, contamination was detected all the way to ground surface. In the upriver portion of the network treated in 2011, no contamination was detected in the injection wells that were drilled through the backfilled 100-N-65 petroleum burn excavation, most likely because clean uncontaminated sediment would have been used to backfill the burn pit (Figure 1-7a). This area along the shoreline also contains the lowest strontium-90 contamination in the groundwater plume. In the downriver portion of the network treated in 2011, contamination was detected during drilling in about half of the injection wells, those closest to the original apatite barrier (Figure 1-7c and Figure 1-7d). The original barrier well network was installed within the channel providing the preferential contaminant pathway to the river. Contamination was not detected during drilling of the downriver treated injection wells furthest from the original barrier network.

The expansion wells were installed systematically with alternating screen depths in accordance with DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*, to target future injections to intervals either within the Hanford formation (shallow screened wells) or within the deeper Ringold Formation (deeper screened wells) (Figure 1-7). The shallow and deep well depths were determined primarily from the geologic Hanford-Ringold contact depth observed at the original barrier (Figures 1-7b and 1-7c). However, based on the detailed hydrogeology gleaned from the expansion borehole descriptions, it appears that the Hanford-Ringold contact elevations upriver and downriver are much shallower than the contact elevations observed along the original barrier. Along the expanded barrier network, the Hanford formation is very shallow; most of the shallow and deep wells are actually screened within the Ringold Unit E. There is still some uncertainty about the elevation of the contact boundary due to similarities in Hanford and Ringold sediment types and the gradational nature of the geologic deposits, but the available data indicate that the contact is much shallower than at other locations along the river. The highest strontium-90 groundwater concentrations near the shoreline are at the location of the original barrier where the Hanford-Ringold contact is lowest, forming a preferential groundwater flow channel in the saturated Hanford sediment.

Although the wells are not screened within alternating Hanford formation and Ringold Formation sediment as originally designed, the new wells do capture the key saturated interval containing most of the detected radiological contamination (assumed coincident with strontium-90 contamination) (Figure 1-7). The deeper screened wells are constructed to treat the saturated interval at the low water table elevation, and the shallower screened wells are constructed to treat the saturated interval at and just below the average water table elevation. Studies and characterization data indicate that most of the relatively immobile strontium-90 contamination occurs within a vertical interval that bounds the average water table (approximately 119 m elevation). This is also supported by the maximum detected contamination data presented on the detailed cross section (Figure 1-7). As determined by previous investigators, data from soil borings collected along the riverbank indicate that strontium-90 concentrations in soil reach a maximum near the mean water table elevation and then decrease with depth (Section 2.2 of PNNL-SA-70033, *100-NR-2 Apatite Treatability Test FY09 Status: High Concentrations Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization: Interim Report*). As a result, the alternating well screen placement (Figure 1-7) adequately bounds the region of water table

fluctuation and the most likely interval of strontium-90 contamination in groundwater and is suitable for treating the strontium-90 plume moving toward the Columbia River.

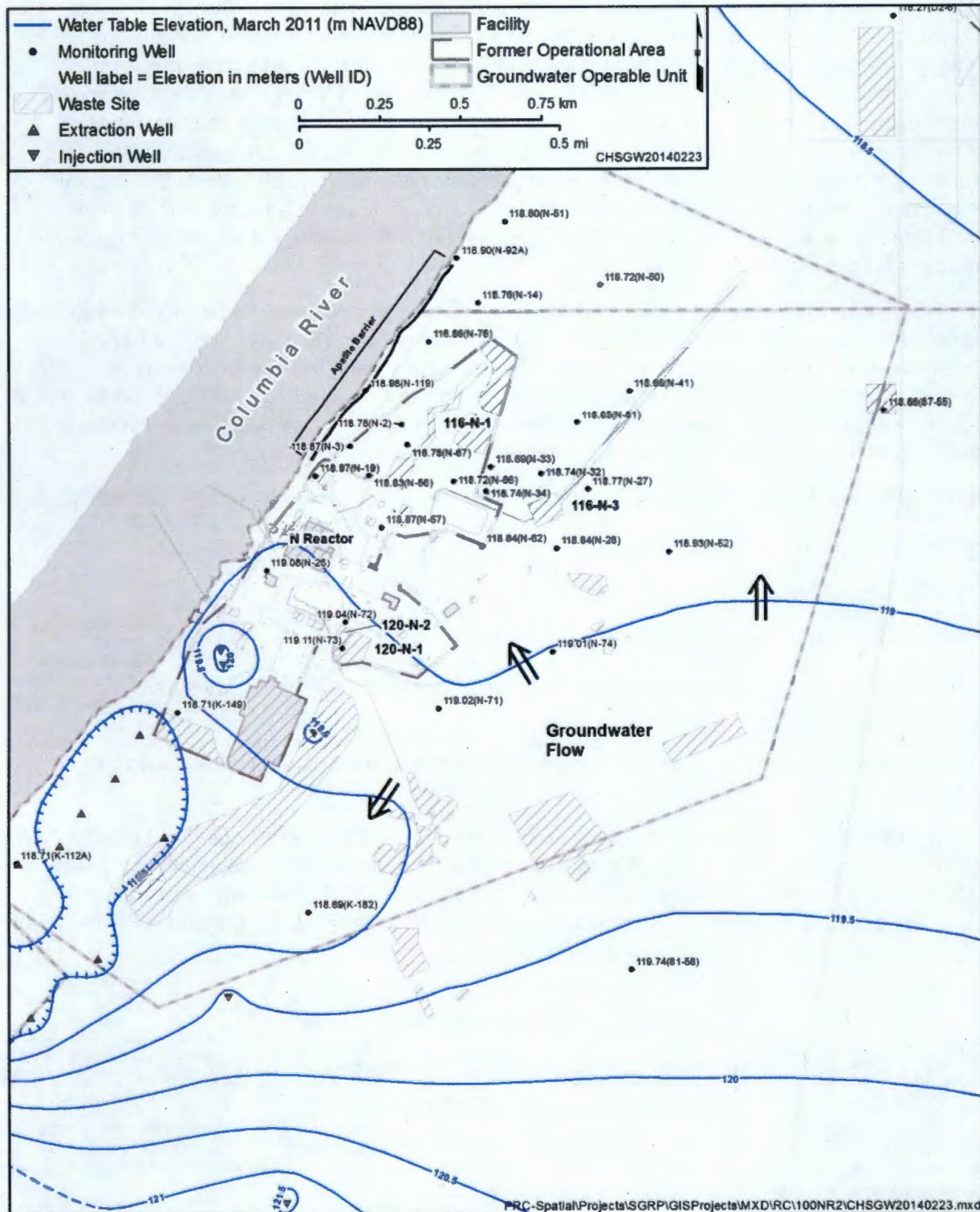
Because the texture of the sediments in the upper stratigraphic units forming the vadose zone and uppermost unconfined aquifer (Ringold Unit E, Hanford formation, and backfill) is so similar (i.e., sandy gravel), distinguishing between these units is sometimes uncertain. Furthermore, the boundaries between these units are not always discrete, but instead often grade into one another as a result of the sediment reworking and mixing during deposition. Although the formation contact depths remain somewhat uncertain, the geologic cross section depicted in Figure 1-7 represents the working hydrogeologic conceptual model for the apatite barrier.

Fluctuations in river stage resulting from seasonal variations and daily operations of Priest Rapids Dam, located 29 km (18 mi) upriver of 100-N, have a significant impact on groundwater flow direction, hydraulic gradient, and groundwater levels near the river (Section 1.4 of PNNL-17429). The volume of water moving in and out of the unconfined aquifer on both a daily and seasonal basis is an order of magnitude greater than groundwater flowing as a result of the regional hydraulic gradient. With the changing direction of groundwater flow, pore water velocities near the river may exceed 10 m/day (32.8 ft/day) (HydroGeoLogic, Inc., 1999, *Groundwater-River Interaction in the Near River Environment at the 100-N Area*). During the high river stage, river water moves into the bank and mixes with groundwater. The zone of mixing is restricted to within tens of meters of the shoreline. During low river stage, this bank storage water drains back into the river and may be observed as springs along the riverbank during rapid drops in river elevation. Springs, seeps, groundwater upwelling, and subsurface discharge along the Columbia River bank are the primary pathway of 100-N groundwater contaminants to the Columbia River. Additional details on the extent of seasonal and daily changes in river stage at the site from Priest Rapids Dam discharge are provided in PNNL-17429.

Beneath the primary strontium-90 waste sites (116-N-1 and 116-N-3), groundwater flows in a north-northwesterly direction most of the year and discharges to the Columbia River, as shown in Figure 1-8, although flow is reversed (river water flows into the aquifer) for short periods during high river stage. The groundwater gradient varies from 0.0005 to 0.003 m/m (Section 1.2 of DOE/RL-2005-96). Near the 116-N-1 and 116-N-3 waste sites, average groundwater velocities are estimated to be between 0.03 and 0.6 m/day (0.1 and 2 ft/day), where 0.3 m/day (1 ft/day) is generally considered typical. However, groundwater flows near the river are significantly influenced by both the diurnal (daily) and seasonal variability in Columbia River stage, as discussed in this subsection.

1.2.3 Site History and Previous Remedial Actions

Construction of the 105-N Reactor began in 1959 (Table 1-1). It was designed and constructed as a dual purpose system to produce plutonium for defense purposes and steam for public/commercial electrical power generation by the Hanford Generating Plant. A major design change from the other eight Hanford production reactors was introduced with the 105-N Reactor to support this dual purpose mission. The once-through cooling water design of previous Hanford reactors was replaced with a closed-loop recirculation design for the primary cooling water system. Heat exchangers (steam generators) in the primary cooling water loop transferred energy to a secondary steam/water cooling system. The primary loop provided cooling for the 105-N Reactor fuel elements and cast-iron thermal shields, transferring the heat to a secondary cooling loop that transferred the excess reactor heat to the Hanford Generating Plant steam generators to generate electricity for commercial use (DOE/RL-91-59, *Closure Report for N Reactor*) or to the Columbia River through a permitted wastewater discharge. The 105-N Reactor operated from 1964 to 1987.



Source: NAVD88, North American Vertical Datum of 1988.

Figure 1-8. 100-NR-2 Operable Unit Water Table (March 2011)

In 1989, the U.S. Environmental Protection Agency (EPA) placed wastes sites within the 100 Area on the National Priorities List (NPL) (40 CFR 300, "National Oil and Hazardous Substances Pollution Contingency Plan," Appendix B) pursuant to the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA). The NPL (40 CFR 300, Appendix B) represents the nation's highest ranked hazardous waste sites prioritized based on their known or potential threat to release hazardous substances, pollutants, or contaminants to the environment and guides EPA in determining waste sites that warrant further investigation. In the same year, EPA, the U.S. Department of Energy (DOE), and the Washington State Department of Ecology (Ecology), known as the Tri-Parties, signed the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al., 1989a) to provide a framework for cleanup of the Hanford Site.

Activities to reduce the flux of strontium-90 to the Columbia River from past-practice liquid waste disposal to waste sites 116-N-1 and 116-N-3 have been underway since the early 1990s in 100-N. Termination of all liquid discharges to the ground by 1993 was a major step toward meeting this goal. However, residual strontium-90 adsorbed on aquifer and periodically rewetted zone sediments beneath the liquid waste disposal sites and extending beneath the near-shore riverbed remained as a continuing source of strontium-90 contamination to groundwater and the Columbia River.

Between 1995 and 2011, the following five strontium-90 groundwater remediation activities took place:

- Implementation of pump-and-treat technology (1995 to 2005)
- Evaluation of alternative treatment technologies (1999 to 2004)
- Treatability testing of an apatite PRB (2006 to 2009)
- Implementation of the DOS to expand the barrier and evaluate and recommend process improvements (2011)
- Evaluation of treatment technologies in the remedial investigation (RI)/feasibility study (FS) (2010 to 2013)

These activities are summarized in the following five subsections of this report. Additional details regarding the strontium-90 remediation history and evaluation of treatment technologies are available in Sections 1.5 and 1.6 of DOE/RL-2010-29; Section 1.1.3 of SGW-47062, *Treatability Test Report for Field-Scale Apatite Jet Injection Demonstration for the 100-NR-2 Operable Unit*; Sections 1.4 and 1.5 of DOE/RL-2005-96; and Section 1.3.5 of DOE/RL-2012-15.

Table 1-1. Chronology of 100-N Key Events

Date	Milestone
May 13, 1959	Construction of the 105-N Reactor begins.
September 1963	Construction of the Hanford Generating Plant begins.
December 1963	105-N Reactor goes into production.
1963	116-N-1 crib and trench activated.
January 1964	105-N Reactor reaches full power.
October 1972	Sodium dichromate replaced with hydrazine for cooling water corrosion control.

Table 1-1. Chronology of 100-N Key Events

Date	Milestone
1982	Increased strontium-90 concentrations measured at N-Springs.
1983	Replacement 116-N-3 crib activated.
1985	Strontium-90 concentration in N-Springs reaches 5,000 pCi/L.
September 1985	Replacement 116-N-3 trench activated. Original 116-N-1 crib and trench deactivated.
December 12, 1986	105-N Reactor placed in stand-down status.
February 1988	105-N Reactor placed in cold standby.
1989	105-N Reactor defueled, irradiated fuel shipped to 100-K Fuel Storage Basins.
October 1991	105-N Reactor ordered shut down; 116-N-3 trench deactivated.
1993	Termination of all liquid discharges to ground.
1995	100-NR-2 OU pump-and-treat system online.
1999	100-N Interim Action ROD issued; evaluation of technologies for strontium-90 removal initiated in accordance with the interim ROD.
2004	Letter report on evaluation of strontium-90 treatment technologies presented at public meeting.
2006	100-NR-2 OU pump-and-treat system placed in standby mode.
2006	Strontium-90 TTP issued (DOE/RL-2005-96, Rev. 0 Reissue).
2006-2007	Treatability testing of low concentration apatite solution (groundwater PRB) in accordance with TTP.
2008	Treatability testing of high concentration apatite solution (groundwater PRB) in accordance with TTP Addendum 1 (DOE/RL-2005-96-ADD1).
2009	Treatability testing of water infiltration in accordance with TTP Addendum 2 (DOE/RL-2005-96-ADD2).
2009	Treatability testing of jet injections (vadose zone PRB) in accordance with TTP Addendum 3 (DOE/RL-2005-96-ADD3).
2009-2010	Installation of injection and monitoring wells to extend the length of the PRB well network from 91 m (300 ft) to 762 m (2,500 ft).
2010	<i>Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan, Addendum 5: 100-NR-1 and 100-NR-2 Operable Units</i> , Rev. 0 approved (DOE/RL-2008-46-ADD5).
2010	Amended 100-N Interim Action ROD for expansion of groundwater PRB length to 762 m (2,500 ft), and addition of jet injections for vadose zone PRB (EPA, 2010).
2011	Expansion of groundwater PRB to 274 m (900 ft) length in accordance with design optimization study (DOE/RL-2010-29).
2011	Drilling and sampling of 8 RI wells.

Table 1-1. Chronology of 100-N Key Events

Date	Milestone
2013	RI/FS Report for 100-NR-1 and 100-NR-2 Operable Units Draft A issued for review (DOE/RL-2012-15).
2014	<i>Remedial Design/Remedial Action Work Plan for the 100-NR-2 Operable Unit</i> (DOE/RL-2001-27), Rev. 1 issued.

Note: Complete citations for references listed in table are provided in Chapter 5.

Table is modified from DOE/RL-90-22, *RCRA Facility Investigation/Corrective Measures Study Work Plan for the 100-NR-1 Operable Unit, Hanford Site, Richland, Washington*.

FS = feasibility study

PRB = permeable reactive barrier

RI = remedial investigation

ROD = record of decision

TTP = treatability test plan

1.2.3.1 Implementation of Pump-and-Treat Technology (1995 to 2005)

In 1995, the *Limited Field Investigation Report for the 100-NR-2 Operable Unit: Hanford Site, Richland, Washington* (DOE/RL-93-81,) was published. Based on the data presented, a qualitative risk assessment was conducted. The qualitative risk assessment indicated that groundwater contaminants in the 100-NR-2 OU exceeded human health risk levels, prompting an expedited response action to address strontium-90 in groundwater along the Columbia River shoreline.

In response to the Action Memorandum issued in 1994 (Ecology and EPA, 1994, "Action Memorandum: N Springs Expedited Response Action Cleanup Plan, U.S. Department of Energy Hanford Site, Richland, WA"), an expedited response action was implemented at N-Springs, where the discharges to the 116-N-1 and 116-N-3 waste sites resulted in contaminated riverbank seeps after 105-N Reactor operations began. The Action Memorandum (Ecology and EPA, 1994) required installation and operation of a pump-and-treat system and construction of a grouted-hinge sheet pile wall at the river's edge by September 1995.

In December 1994, DOE conducted a sheet pile installation test program. It was concluded that the Ringold Formation was not penetrable with standard sheet pile installation methods, and a sheet pile barrier could only be installed after the in situ material was broken up and loosened before pile driving. In March 1995, the Tri-Parties agreed that the sheet pile wall could not be installed as specified in the Action Memorandum (Stanley and Sherwood, 1995, "Re: USDOE Request to Change N Springs Action Memorandum").

The 100-NR-2 OU pump-and-treat system was completed by August 1995 and was in full operation by September 1995. The system was originally designed to have a minimum combined extraction pumping rate of 190 L/min (50 gal/min) with a 10-year operational life (BHI-00030, *N Springs Groundwater Pump-and-Treat System Functional and Operational Requirements*). Based on recommendations in DOE/RL-95-100, *N-Springs Expedited Response Action Performance Evaluation Report*, and DOE/RL-97-34, *N-Springs Pump and Treat System Optimization Study*, the system was upgraded to operate at 227 L/min (60 gal/min) beginning in December 1996.

The pump-and-treat well network consisted of four extraction wells (199-N-75, 199-N-103A, 199-N-105A, and 199-N-106A) and two injection wells (199-N-29 and 199-N-104A), as depicted on

Figure 1-9. The treatment skid used clinoptilolite to remove strontium-90 from the extracted groundwater prior to injection back to the aquifer. The pump-and-treat system operated from September 1995 through March 2006, treating more than 1.1 billion L (305 million gal) of groundwater and removing approximately 1.8 Ci of strontium-90 from the aquifer (DOE/RL-2008-66, *Hanford Site Groundwater Monitoring for Fiscal Year 2008*). The 0.2 Ci of strontium-90 removed each year by the pump-and-treat system was estimated to be 10 times less than the amount removed by natural radioactive decay (DOE/RL-2004-21, *Calendar Year 2003 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit (OU) Pump & Treat Operations*). Strontium-90 data collected at the river's edge showed that concentrations had not decreased. Although the pump-and-treat system may have met the objective of reducing the flow of groundwater in the strontium-90 plume area to the river, it did not meet the objective of reducing strontium-90 concentrations in aquifer pore fluid at the shoreline or in the bank storage zone. Based on the pump-and-treat system's limited effectiveness in removing strontium-90 from within these zones and the need for ambient conditions to test a PRB, the Tri-Parties approved placing the system in standby mode in March 2006 (M-16-06-01, *Federal Facility Agreement and Consent Order Change Control Form: Establish Interim Milestone M-016-14, Complete Construction of a Permeable Reactive Barrier at 100-N*).

1.2.3.2 Evaluation of Alternative Treatment Technologies (1999-2004)

An Interim Action Record of Decision (ROD) was issued by EPA in 1999 (EPA/ROD/R10-99/112) that required DOE to conduct a comprehensive review of strontium-90 treatment technologies to complement the existing interim remedial actions. This review was commissioned under the DOE Innovative Treatment & Remediation Demonstration (ITRD) program, and the results were presented in *Hanford 100-N Area Remediation Options Evaluation Summary Report* (ITRD, 2001). Based on the evaluation presented in that document, the technical advisory group recommended that monitored natural attenuation, soil flushing, phytoremediation, stabilization by phosphate injection (apatite), impermeable barriers (sheet pile and cryogenic), and treatment barriers (clinoptilolite) be evaluated further for strontium-90 remediation. Subsequent evaluations and field trials led to the elimination of soil flushing and sheet pile barriers as viable technologies for the 100-NR-2 OU.

A letter report (FH and CH2M HILL, 2004, *Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit*) was submitted to DOE in October 2004. Alternatives evaluated in the letter report included PRBs, impermeable barriers, monitored natural attenuation, and phytoremediation. The letter report recommended that the aqueous injection PRB be the first technology to test in the field. This letter report and related public workshop comments (December 2004), together with the 2001 ITRD report, contributed to the technology evaluation requirement specified in the Interim Action ROD (EPA/ROD/R10-99/112). In 2006, the Tri-Parties agreed that the long-term strategy for groundwater remediation at 100-N should include apatite sequestration as the primary treatment technology (DOE/RL-2006-20, *The Second CERCLA Five-Year Review Report for the Hanford Site*).

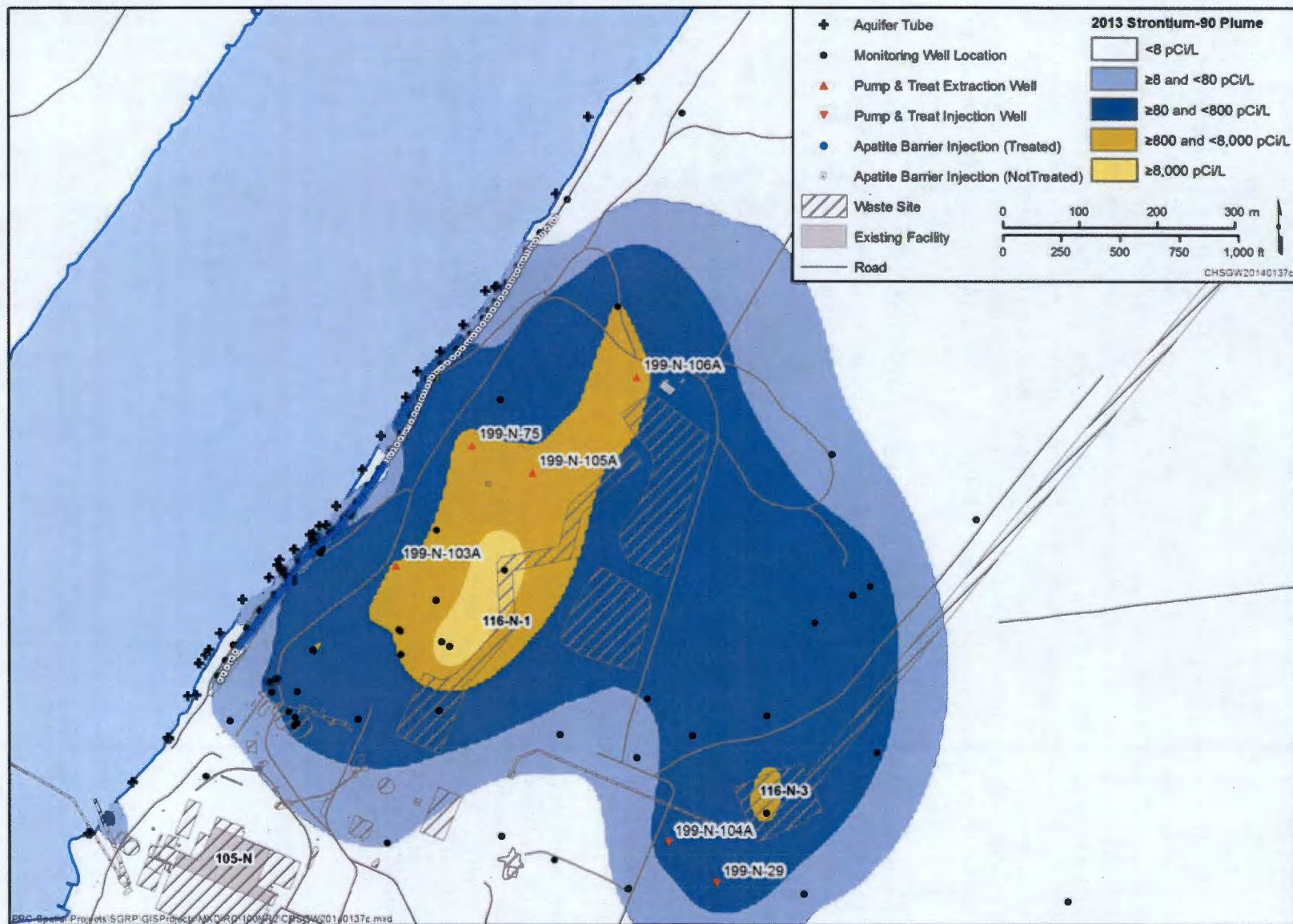


Figure 1-9. Location of the 100-NR-2 Operable Unit Pump-and-Treat Extraction and Injection Wells

1.2.3.3 Treatability Testing of an Apatite Permeable Reactive Barrier (2006 to 2009)

To field test the aqueous injection PRB for sequestration of strontium-90, a treatability test plan (TTP) was approved in March 2006 (DOE/RL-2005-96). During the treatability test, a low concentration aqueous apatite solution was injected into a 91 m (300 ft) long linear array of wells located within the highest groundwater strontium-90 concentrations along the shoreline. Three addenda to the TTP were issued between June 2008 and November 2009, each outlining additional testing to evaluate apatite emplacement methods or treatment areas. The first addendum to DOE/RL-2005-96, issued in 2008, was a field test instruction for injection of a high concentration aqueous apatite solution. The second addendum to DOE/RL-2005-96, issued in 2009, was the plan for conducting a preliminary field-scale water infiltration experiment in the vicinity of the apatite treatability test site. The third addendum (DOE/RL-2005-96, Addendum 3) was the plan for conducting a preliminary field-scale demonstration to evaluate jet injection of three different media: a phosphate solution, pre-formed apatite, and the same phosphate solution followed by the addition of pre-formed apatite. The results of these field tests are provided in the reports listed in Table 1-2. The timeline for activities conducted in accordance with the TTP is provided in Table 1-3.

Table 1-2. 100-NR-2 Operable Unit Treatability Test Plans and Reports

Test Plan	Test Plan Report
DOE/RL-2005-96	PNNL-17429
DOE/RL-2005-96-ADD1	PNNL-19572, PNNL-20252
DOE/RL-2005-96-ADD2	PNNL-18303, PNNL-20322
DOE/RL-2005-96-ADD3	SGW-47062, PNNL-19524

Note: Complete reference citations are provided in Chapter 5.

Table 1-3. 100-NR-2 Operable Unit Apatite Permeable Reactive Barrier Timeline

Year	Dates	PRB Wells ^a	Description of Field Activity	Injection Chemistry
2005	Oct 11 to Oct 12	N-122, N-123	Apatite PRB monitoring wells installed to provide characterization data and screened across the lower Hanford formation and upper Ringold Formation	
2006	Feb 10 to Mar 27	N-136, N-137, N-138, N-139, N-140, N-141, N-142, N-143, N-144, N-145	Apatite PRB injection wells installed and screened across the lower Hanford formation and upper Ringold Formation on 9.1 m spacing between wells	
2006	Feb 27 to Mar 30	N-146, N-147	Apatite PRB monitoring wells installed and screened across the lower Hanford formation and upper Ringold Formation	
2006	May 03	N-138	Tracer test at the pilot test #1 location (upriver end of PRB)	sodium bromide (NaBr)

Table 1-3. 100-NR-2 Operable Unit Apatite Permeable Reactive Barrier Timeline

Year	Dates	PRB Wells ^a	Description of Field Activity	Injection Chemistry
2006	May 31 to Jun 01	N-138	Hanford formation/Ringold Formation injection at high river level at the pilot test #1 location (upriver end of PRB)	4 mM Ca, 10 mM citrate, 2.4 mM PO ₄
2006	Sep 27 to Sep 28	N-137	Ringold Formation injection at low river level at the pilot test #2 location (downriver end of PRB)	2 mM Ca, 5 mM citrate, 2.4 mM PO ₄
2006 - 2007	Nov 13 to Feb 15	N-122, N-123, N-146, N-147	Performance monitoring	
2007	Feb 28 to Mar 02	N-136, N-142, N-145 ^b	Low concentration injections into Ringold Formation at low river level	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007	Mar 02 to Mar 05	N-140, N-144	Low concentration injections into Ringold Formation at low river level	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007	Mar 20 to Mar 23	N-137, N-141	Low concentration injections into Hanford formation and Ringold Formation at high river level	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007	Mar 23 to Mar 25	N-139, N-143	Low concentration injections into Hanford formation and Ringold Formation at high river level	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007	Jun 05 to Jun 06	N-136, N-142, N-144	Low concentration injections into Hanford formation at high river level (Pilot Test #3, Phases I and II)	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007	Jun 08 to Jun 10	N-138	Low concentration injections into Hanford formation at high river level (Pilot Test #3, Phase III)	1 mM Ca, 2.5 mM citrate, 10 mM PO ₄
2007 - 2008	Jun 10 to Jun 03	N-122, N-123, N-146, N-147	Performance monitoring	
2008	Mar 25 to May 23	N-159, N-160, N-161, N-162, N-163, N-164	Apatite PRB injection wells installed and screened in the upper Ringold Formation on 4.6 m spacing between wells N-137 and N-141	
2008	Jun 04 to Jun 06	N-137, N-138, N-159	High concentration injections into Hanford formation and Ringold Formation at higher river level (High Concentration Injection #1)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2008	Jun 26 to Jun 28	N-141, N-145, N-161	High concentration injections into Hanford formation and Ringold Formation at higher river level (High Concentration Injection #2)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2008	Jun 30 to Jul 03	N-139, N-143, N-163	High concentration injections into Hanford formation and Ringold Formation at higher river level (High Concentration Injection #3)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄

Table 1-3. 100-NR-2 Operable Unit Apatite Permeable Reactive Barrier Timeline

Year	Dates	PRB Wells ^a	Description of Field Activity	Injection Chemistry
2008	Jul 14 to Jul 17	N-136, N-142, N-160, N-164	High concentration injections into Hanford formation and Ringold Formation at lower river level (High Concentration Injection #4)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2008	Jul 22 to Jul 24	N-140, N-144, N-162	High concentration injections into Hanford formation and Ringold Formation at lower river level (High Concentration Injection #5)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2008	Jul 24 to Dec 08	N-122, N-123, N-146, N-147	Performance monitoring	
2009	Feb 04, May 26, Aug 13, Nov 20	N-122, N-123, N-146, N-147	Performance monitoring	
2009	Dec 04 to Dec 09	C7700 through C7705	Jet injection drive points installed in south grid (northwest of Well 199-N-217) for phosphate injection	
2009	Dec 11 to Dec 15	C7706 through C7711	Jet injection drive points installed in center grid (between Well 199-N-219 and Well 199-N-220) for apatite and phosphate injection	
2009	Dec 16 to Dec 17	C7712 through C7717	Jet injection drive points installed in north grid (northeast of Well 199-N-222) for apatite injection	
2009 - 2010	Oct 16 to Apr 23	N-200 through N-345 ^c	Apatite PRB injection wells installed upriver and downriver of the original 91 m (300 ft) long PRB segment and screened in either the shallow aquifer or deeper in the upper Ringold Formation on 4.6 m spacing	
2009 - 2010	Dec 02 to Apr 21	N-346 through N-367	Apatite PRB monitoring wells installed upriver and downriver of the original 91 m (300 ft) long PRB segment and screened deeper in the upper Ringold Formation	
2009	Oct 30 to Nov 04	N-368, N-369, N-370	Apatite PRB monitoring wells drilled near injection Well 199-N-137 in the original barrier segment approximately one year after high concentration injection to collect post-injection cores to characterize the phosphate and strontium-90 distribution in sediments and screened deeper in the upper Ringold Formation	
2010	Feb 24, May 23, Aug 15	N-122, N-123, N-146, N-147	Performance monitoring	

Table 1-3. 100-NR-2 Operable Unit Apatite Permeable Reactive Barrier Timeline

Year	Dates	PRB Wells ^a	Description of Field Activity	Injection Chemistry
2011	May 02 or Jun 27, Nov 10	N-122, N-123, N-146, N-147	Performance monitoring	
2011	Sep 07 to Sep 09	N-211, N-213, N-215, N-217, N-219, N-221, N-223 N-225, N-227, N-229, N-231, N-233	High concentration injections into deep injection wells at lower river level (upriver barrier extension)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2011	Sep 13 to Sep 15	N-212, N-214, N-216, N-218, N-220, N-222, N-224 N-226, N-228, N-230, N-232, N-234	High concentration injections into shallow injection wells at lower river level (upriver barrier extension)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2011	Sep 21 to Sep 23	N-236, N-238, N-240 N-242, N-244, N-246, N-248 N-250, N-252, N-254, N-256, N-258	High concentration injections into deep injection wells at lower river level (downriver barrier extension)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2011	Sep 23 to Sep 25	N-235, N-237, N-239 N-241, N-243, N-245, N-247 N-249, N-251, N-253, N-255, N-257	High concentration injections into shallow injection wells at lower river level (downriver barrier extension)	3.6 mM Ca, 9.0 mM citrate, 40 mM PO ₄
2011	Sep 16, Sep 28, Oct 13	N-347, N-348, N-349, N-96A	Performance monitoring at upriver segment injected in 2011	
2011	Sep 27, Oct 12, Oct 27	N-350, N-351, N-352, N-353	Performance monitoring at downriver segment injected in 2011	
2012	May 06 or 07 or 09, Sep 26 or 27 or Oct 01	N-122, N-123, N-146, N-147, N-347, N-348, N-349, N-96A, N-350, N-351, N-352, N-353	Performance monitoring at treated segments of apatite PRB	
2013	May 06, Sep 06 ^d	N-122, N-123, N-146, N-147, N-347, N-348, N-349, N-96A, N-350, N-351, N-352, N-353	Performance monitoring at treated segments of apatite PRB	

Table 1-3. 100-NR-2 Operable Unit Apatite Permeable Reactive Barrier Timeline

Year	Dates	PRB Wells ^a	Description of Field Activity	Injection Chemistry
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Source: Updated from DOE/RL-2011-01, *Hanford Site Groundwater Monitoring Report for 2010* (Table 6-3).

a. Well names are prefixed by "199-".

b. Well 199-N-145 replaced Well 199-N-142 part way through injection because of problems with Well 199-N-142.

c. Even numbered wells (from 199-N-200 through 199-N-234) and odd numbered wells (from 199-N-235 through 199-N-345) screened in the shallow aquifer; odd numbered wells (from 199-N-201 through 199-N-233) and even numbered wells (from 199-N-236 through 199-N-344) screened deeper in the aquifer.

d. Wells 199-N-122 and 199-N-123 were sampled on November 11; Well 199-N-147 was sampled on November 13.

PRB = permeable reactive barrier

The TTP outlined field testing to be conducted in two phases: initial field pilot tests, followed by injection of a low concentration solution in the barrier wells to create a 91 m (300 ft) long apatite PRB. The results and evaluation of the pilot tests and the low concentration solution injections are provided in PNNL-17429.

The objectives of the pilot tests were to evaluate and adjust, as necessary, the composition of the injection solution and determine the optimal injection volume per well for a well spacing of 9 m (30 ft). Pilot tests were conducted at both the upriver (southwest) and downriver (northeast) ends of the original barrier (Figure 1-10). A tracer injection test and the first pilot apatite injection test were conducted at the upriver end of the barrier in the spring of 2006 during high-river stage conditions. The second pilot test was conducted at the downriver end of the barrier during low-river stage conditions in September 2006. The monitoring well networks installed at the pilot test sites are shown in Figures 1-11a and 1-11b. As described in Section 5.0 of PNNL-17429, the results from the pilot tests and additional laboratory work led to modifying the injection solution composition, injection volumes, and operational parameters for injection of the barrier wells.

The objective of the low concentration injections was to stabilize the strontium-90 in the aquifer before the planned injections of high concentration solutions for long-term strontium-90 treatment. The final low concentration calcium-citrate-phosphate injection solution consisted primarily of calcium chloride, trisodium citrate, and sodium phosphate (1 mM calcium, 2.5 mM citrate, and 10 mM phosphate) (Section 7.0 of PNNL-17429). Injections in the 10 original barrier wells were conducted during February and March 2007 (during both low- and high-river stage conditions) and July to August 2007 (during high-river stage conditions).

The injection wells within the original barrier section are screened across both the Hanford formation and the Ringold Formation. Data from the treatability test indicated that the apparent permeability contrast between the Hanford and Ringold formations was significantly less over the upriver portion of the barrier and greater over the downriver portion of the barrier (Section 7.3 of PNNL-17429). The lower permeability contrast allowed both the Hanford and Ringold screened intervals to be treated with a single injection operation at high river stage. However, because of the greater contrast downriver, it was recommended that wells in this area be screened only across the Ringold Formation for future injections (Section 9.1 of PNNL-17429).

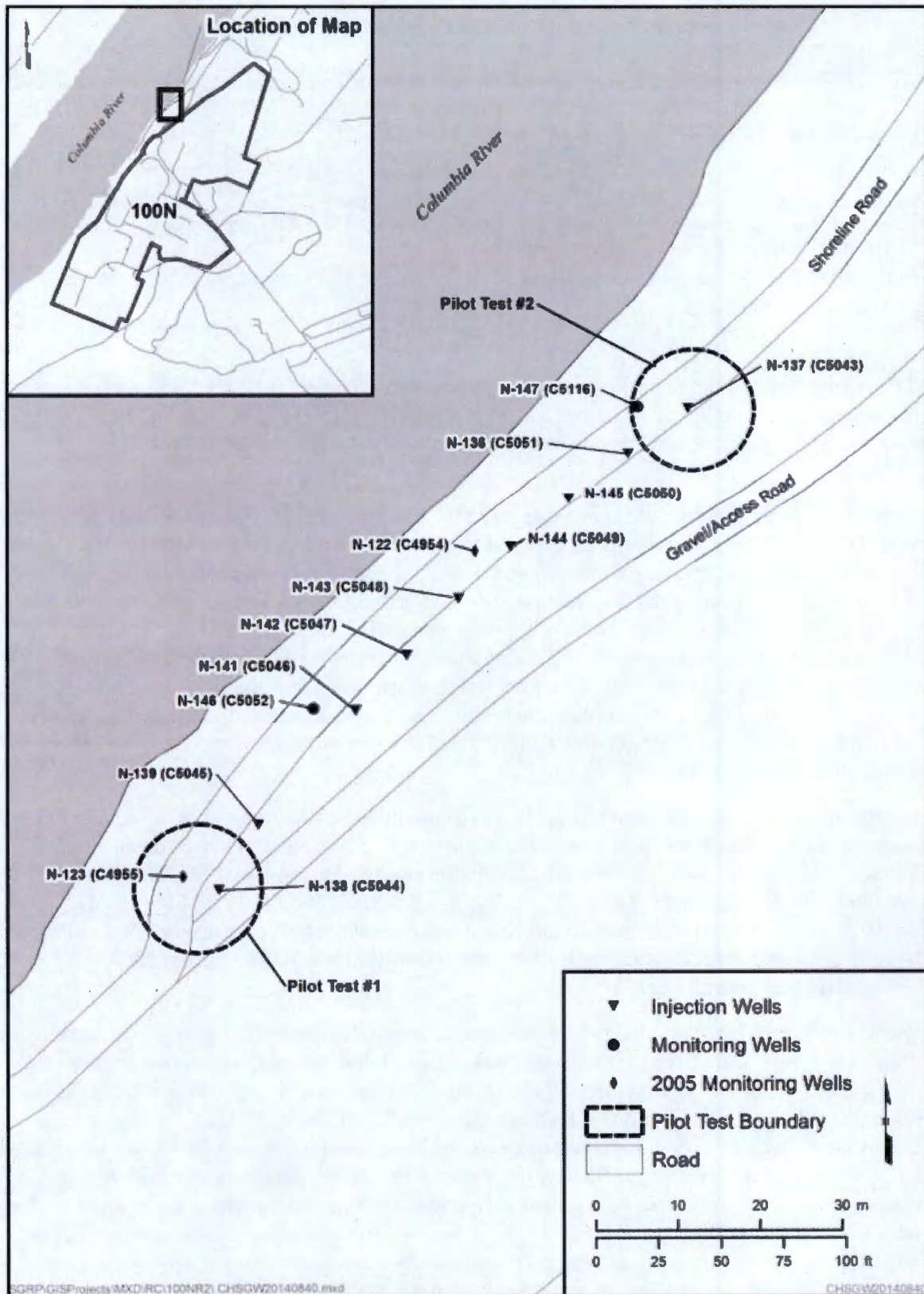


Figure 1-10. Location of Original Apatite Permeable Reactive Barrier and Pilot Tests Conducted in 2006

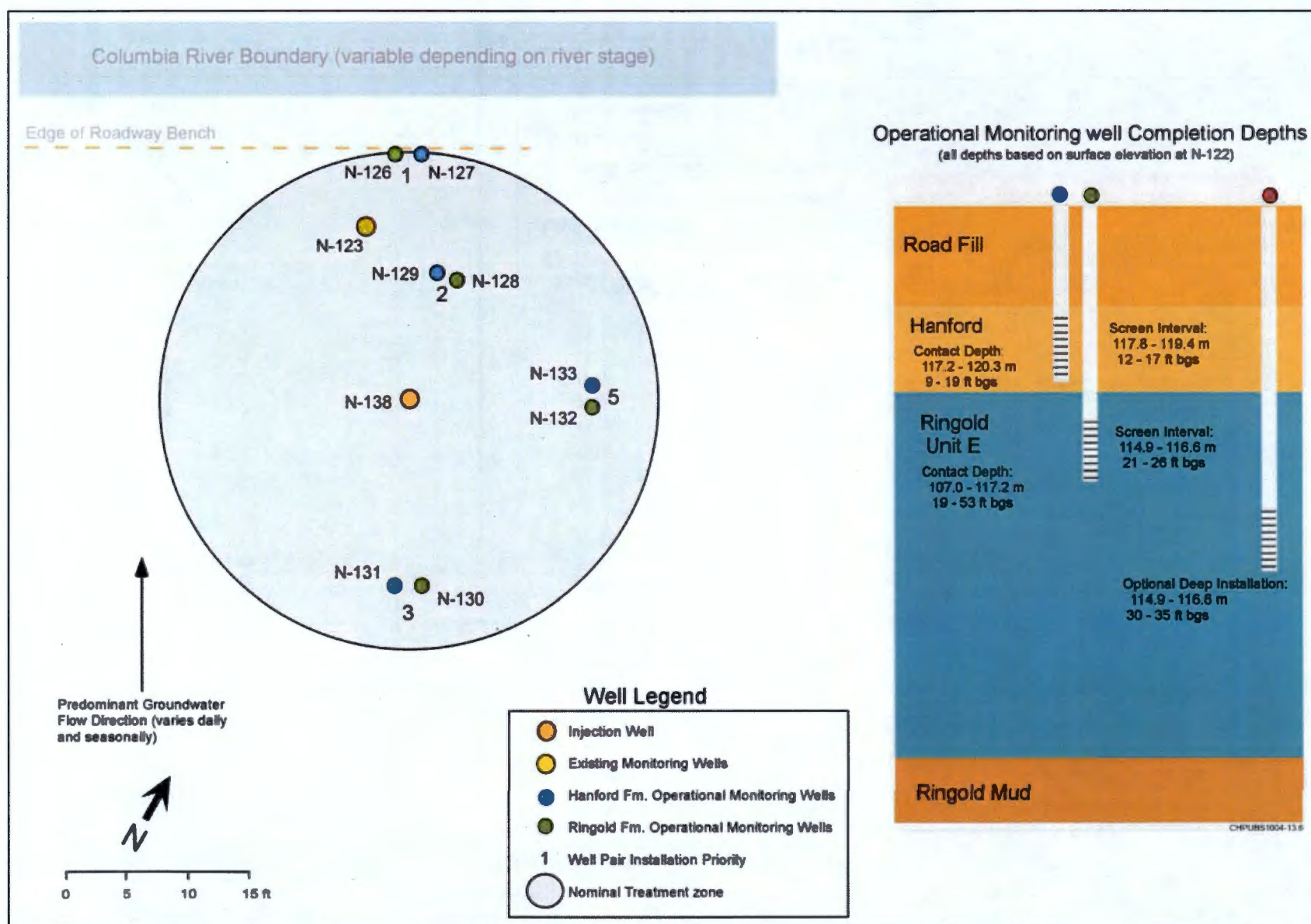


Figure 1-11a. Configuration of Pilot Test 1

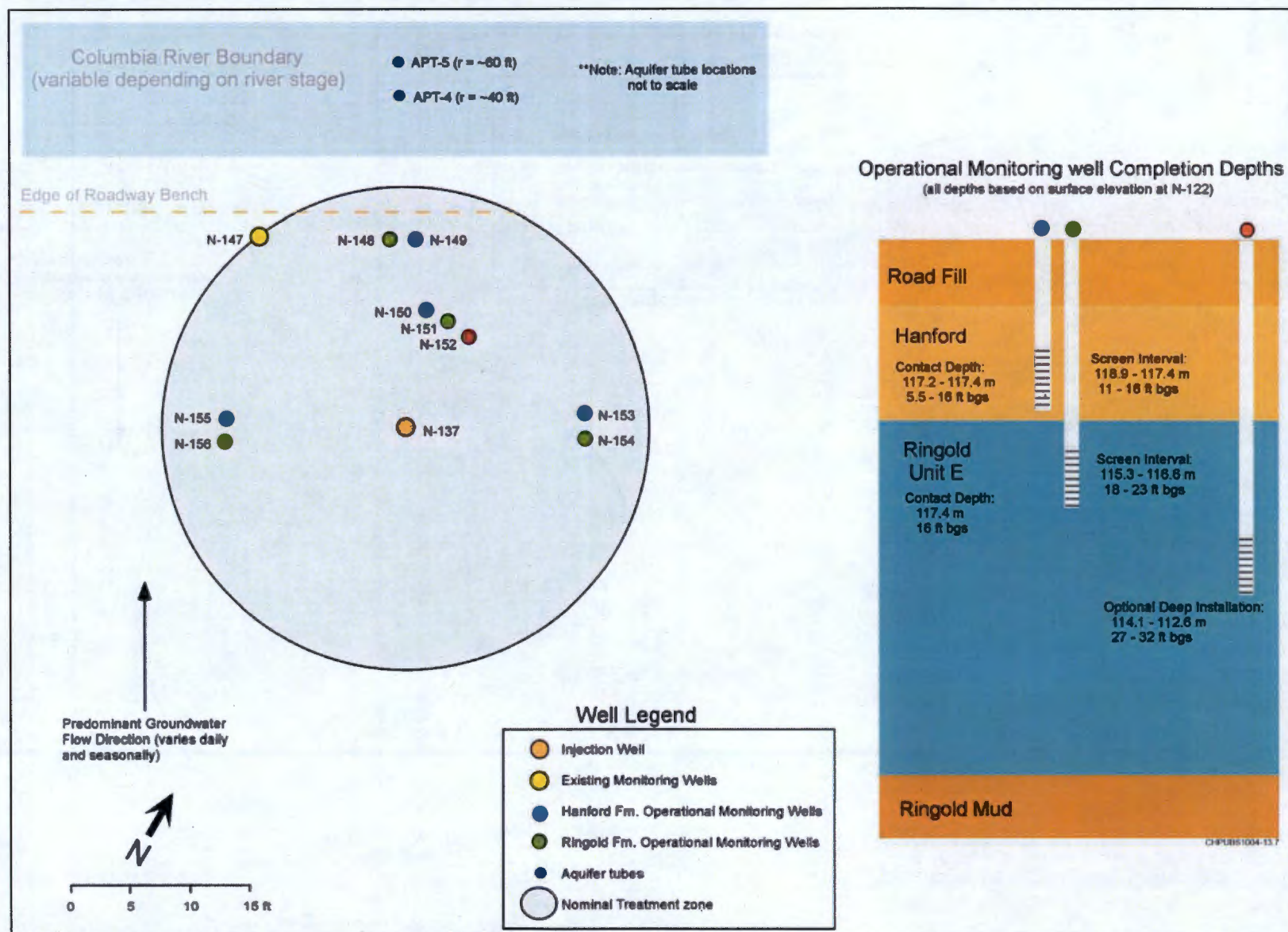


Figure 1-11b. Configuration of Pilot Test 2

In 2008, the high concentration calcium-citrate-phosphate injection solution (3.6 mM calcium, 9.0 mM citrate, and 40 mM phosphate) was injected in wells to treat the original 91 m (300 ft) long PRB in accordance with Addendum 1 to the TTP (DOE/RL-2005-96-ADD1). The pilot test sites used to evaluate the low concentration injections were used again to evaluate the high concentration injections prior to continuing with the remaining barrier well injections. The high concentration solution was injected in 16 wells: the original 10 injection wells were screened in both the Hanford and Ringold formations, and the 6 additional wells were screened only in the Ringold Formation. The results and evaluation of the pilot tests and the high concentration solution injections are provided in PNNL-19572.

Based on the laboratory and field-scale treatability tests, it was determined that the high concentration apatite formulation was the most favorable to minimize the number of injection operations required, minimize short-term increases in strontium-90 and some metals concentrations associated with injection of high ionic strength solutions, and keep injection formulations well below solubility limits to reduce the potential for operational challenges associated with solution stability (Section 5.0 of PNNL-19572).

Based on the high concentration injections, it was recommended that future treatment of the Ringold Formation be conducted in Ringold-only wells at low river stage (not to exceed an elevation of 118 m) (Section 5.0 of PNNL-19572). The Hanford formation injection wells should be treated at high river stage (target elevation of 120 m, minimum elevation of 119 m). Based on the phosphate concentrations measured in soil cores, collected in November 2009, it was recommended that the injection volume for the Hanford formation wells should be 227,000 L (60,000 gal), and the injection volume for the Ringold Formation wells should be 454,000 L (120,000 gal).

Treatability testing of pilot-scale tracer infiltration was conducted in September through November 2010 in accordance with Addendum 2 to the TTP (DOE/RL-2005-96-ADD2). The objectives of the testing were to address strategies for infiltration of aqueous solution from near-ground surface into the vadose zone and the type of monitoring equipment that could be used to monitor the infiltration front. The results are provided in PNNL-20322, *100-NR-2 Apatite Treatability Test: Fall 2010 Tracer Infiltration Test*. The results of laboratory experiments conducted to determine whether the unsaturated Hanford formation is conducive to formation of apatite through surface application of reagents are provided in PNNL-18303, *Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a Ca-Citrate-Phosphate Solution*.

Treatability testing of the jet injection technology to emplace materials in the vadose zone and upper unconfined aquifer was conducted in December 2009 in accordance with Addendum 3 to the TTP (DOE/RL-2005-96-ADD3). The field-scale demonstration was conducted at three locations upriver of the original 91 m (300 ft) long apatite PRB to evaluate potential strategies for jet injection of three different media: a phosphate-only solution, pre-formed apatite (fishbone), and the same phosphate solution with the addition of the pre-formed apatite. The results are provided in SGW-47062. Sediment cores were collected in February 2010 from four wells installed within the demonstration locations during extension of the apatite PRB well network. The sediment core results are provided in PNNL-19524. Results from the sediment cores indicate that jet injection is a viable method for emplacement of phosphate solution and pre-formed apatite in the vadose zone.

Results of performance monitoring at treated portions of the barrier are available in the reports listed in Table 1-4.

Table 1-4. Reports on Performance Monitoring of the Apatite Permeable Reactive Barrier

Year	Report Number	Report Title
2009	PNNL-19572	<i>100-NR-2 Apatite Treatability Test: High-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization</i>
2010	PNNL-20252	<i>100-NR-2 Apatite Treatability Test: An Update on Barrier Performance</i>
2011	DOE/RL-2012-02	<i>Calendar Year 2011 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump-and-Treat Operations, and 100-NR-2 Groundwater Remediation</i>
2012	DOE/RL-2013-13	<i>Calendar Year 2012 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump-and-Treat Operations, and 100-NR-2 Groundwater Remediation</i>

1.2.3.4 Implementation of the Design Optimization Study (2011)

In 2010, the amendment to the 1999 interim action ROD (EPA, 2010, *U.S. Department of Energy 100-NR-1 and NR-2 Operable Units Hanford Site – 100 Area Benton Country, Washington Amended Record of Decision, Decision Summary and Responsiveness Summary*) altered the remedy specified for strontium-90 near the 100-N shoreline, as follows: deploy apatite sequestration technology by extending the apatite barrier from 91 m (300 ft) to approximately 762 m (2,500 ft). The amended ROD (EPA, 2010) specified that the barrier would initially be extended 91 m (300 ft) to the southwest and 91 m (300 ft) to the northeast to optimize the injection well design and apatite solution composition prior to full-scale deployment. The remedy also included decommissioning the existing 100-NR-2 OU pump-and-treat system components.

Between November 2009 and April 2010, 171 wells were installed to extend the length of the apatite barrier well network from 91 m (300 ft) to 762 m (2,500 ft). Of these 171 wells, 146 are injection wells and 25 are performance monitoring wells. Borehole drilling, sampling, and well construction were performed in accordance with DOE/RL-2009-32. The field activities during drilling and construction of the 171 wells are provided in SGW-47791. Figures 1-12 through 1-16 illustrate the general location along the 100-NR-2 OU shoreline of the apatite injection barrier wells, surrounding monitoring wells, and aquifer tubes. Figure 1-7 illustrates the cross sectional detail of the barrier network wells within the unconfined aquifer.

The DOS (DOE/RL-2010-29) was prepared to support deployment and evaluation of the improvements for the delivery and emplacement of apatite-forming chemicals identified during the treatability test. Implementation of the DOS in 2011 resulted in extension of the injected portion of the barrier from 91 m (300 ft) long to 274 m (900 ft) long. The results and evaluation of the solution injections are provided in this report.

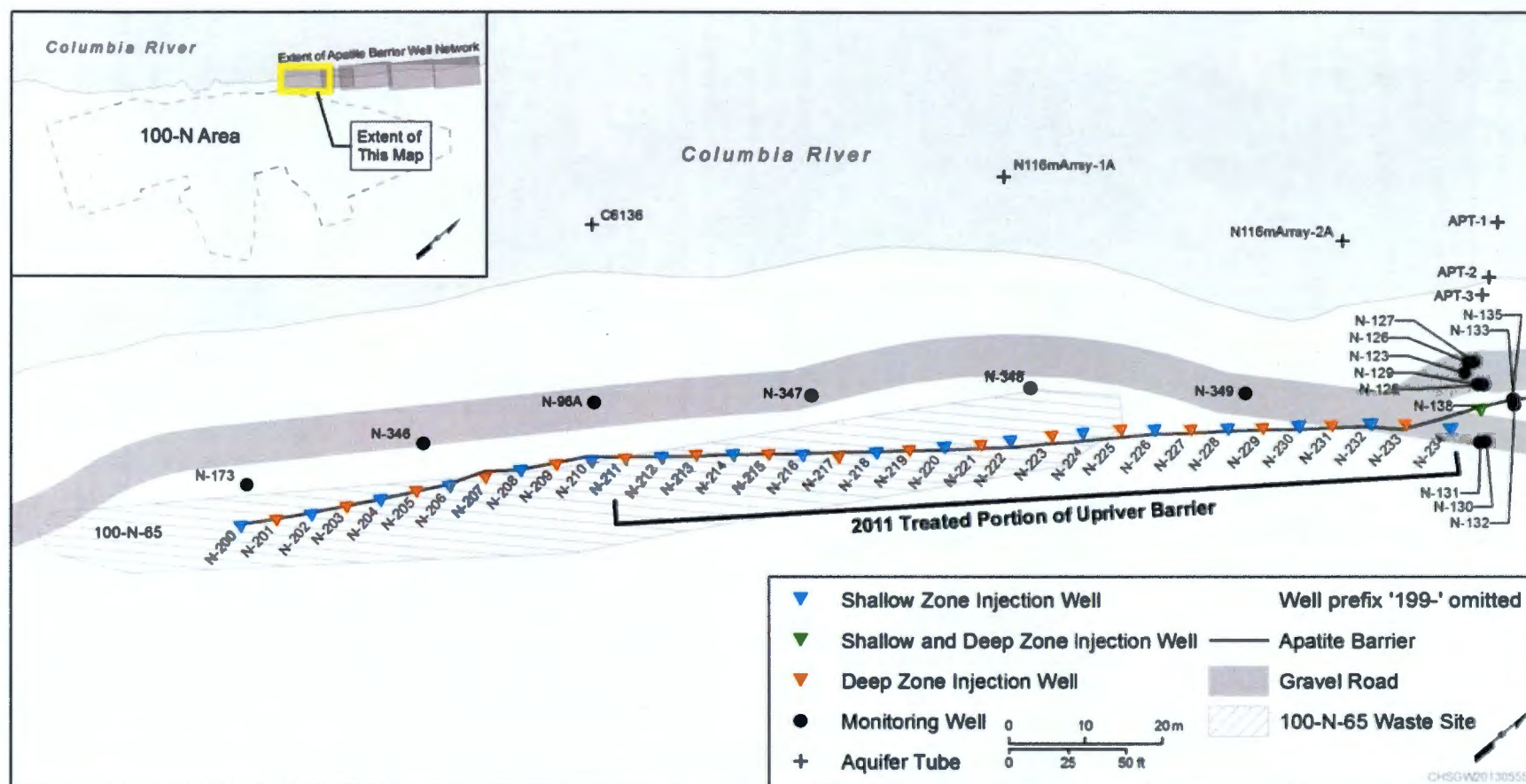


Figure 1-12. Location of Apatite Barrier Wells Upriver of Original Barrier Segment



Figure 1-13. Location of Apatite Barrier Wells in Original Barrier Segment

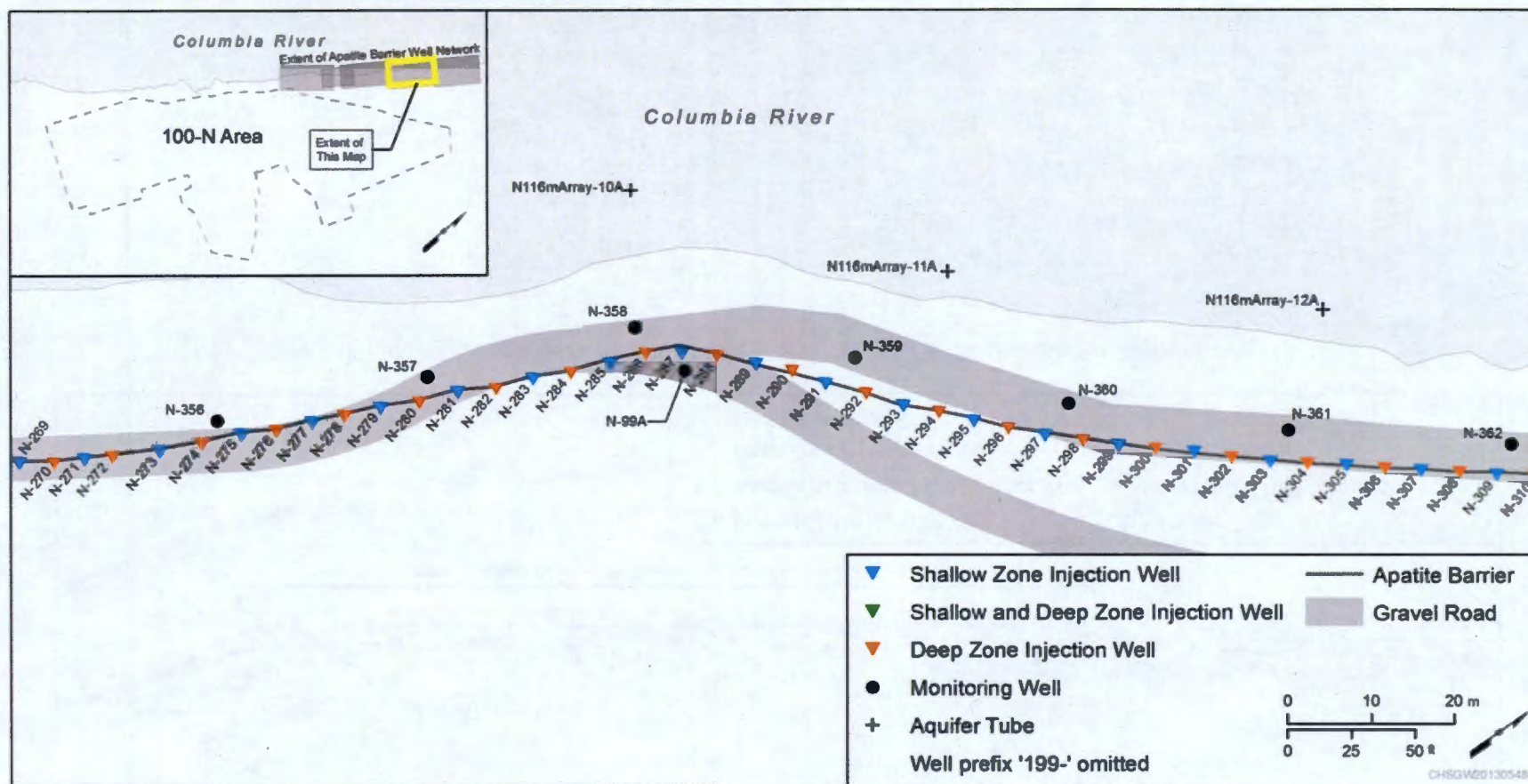


Figure 1-15. Location of Apatite Barrier Wells Downriver of Original Barrier Segment (continued from Figure 1-14)

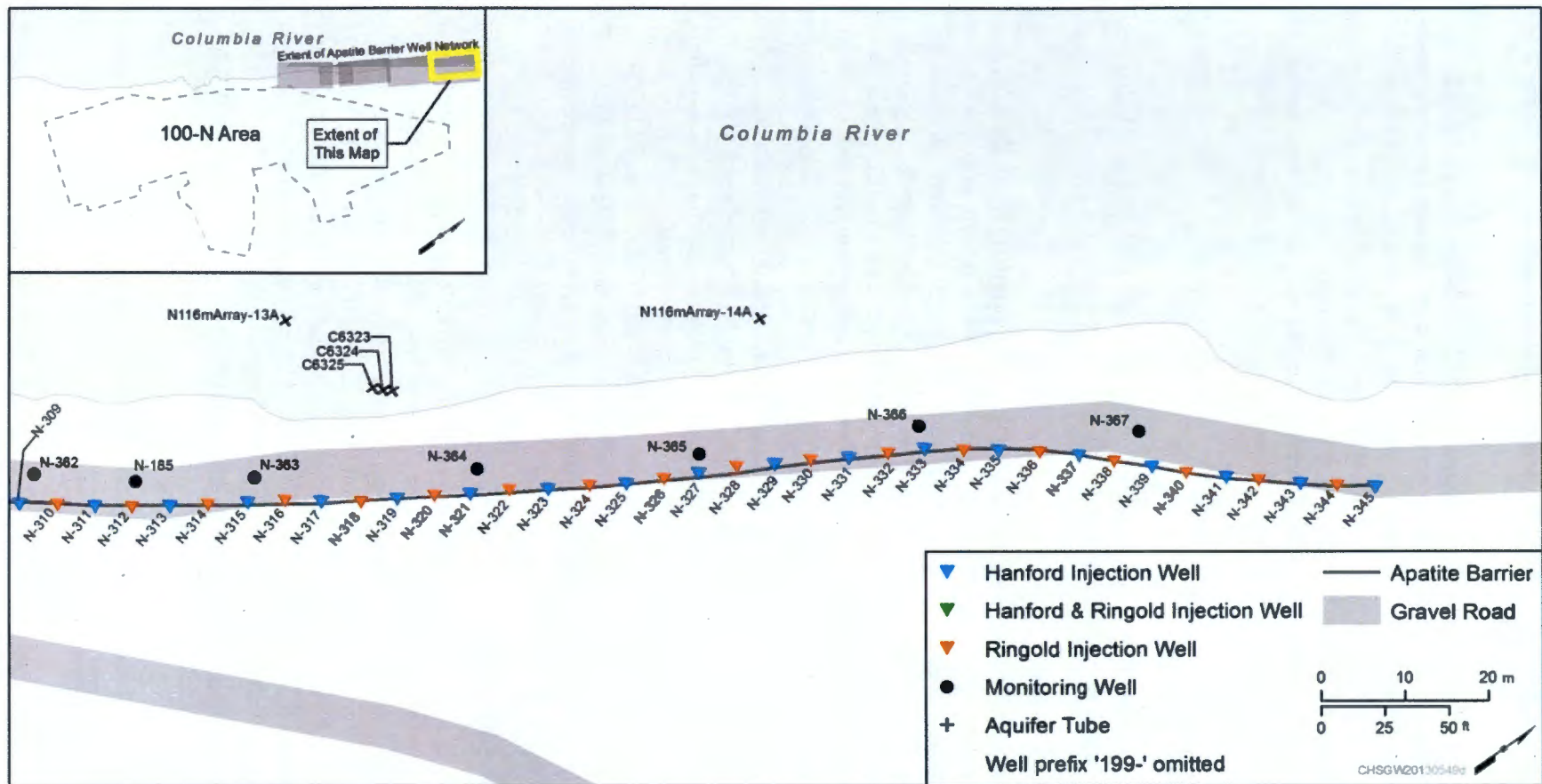


Figure 1-16. Location of Apatite Barrier Wells Downriver of Original Barrier Segment (continued from Figure 1-15)

1.2.3.5 Evaluation of Treatment Technologies in the Remedial Investigation/Feasibility Study (2010-2013)

The RI/FS work plan (DOE/RL-2008-46-ADD5) was developed to identify additional data needed to make an integrated, comprehensive, final action decision for contaminated waste sites and groundwater in 100-N. The RI was conducted in 2011 to resolve the data gaps identified in the work plan. Draft A of the RI/FS report (DOE/RL-2012-15) was submitted in June 2013. With the exception of the required No Action alternative, all of the remedial alternatives in Draft A include treatment (injection) of the remaining wells in the groundwater apatite PRB network to complete the 762 m (2,500 ft) long barrier and creation of a 300 m (1,000 ft) long vadose zone apatite PRB using jet injection (Section 9.2.2 of DOE/RL-2012-15).

1.3 Treatment Technology Description

The following description of the treatment technology is summarized from Section 2 of DOE/RL-2010-29 and Section 2.4 of PNNL-19572, which provide additional details.

1.3.1 General Characteristics of Apatite

Apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is a natural calcium phosphate mineral occurring primarily in the Earth's crust as phosphate rock. It is also a primary component in teeth and bones of animals. Apatite minerals sequester elements into their molecular structures through isomorphic substitution, whereby elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the hexagonal crystal structure. Figure 1-17 shows cationic and anionic substitutions that commonly occur in the apatite structure. The substitution of strontium for calcium in the crystal structure is thermodynamically favorable and will proceed provided the two elements exist.

As indicated on Figure 1-17, stable strontium and other competing cations, especially the divalent transition metals (e.g., cadmium, zinc, iron, lead, and manganese), can also be incorporated in the apatite structure. The average concentrations of stable strontium and competing cations present in groundwater will dictate the mass of apatite needed for long-term sequestration. Recent experiments measuring strontium incorporation in apatite from a solution containing only calcium and strontium, and from groundwater containing calcium and strontium and all transition metals, found no difference in the strontium uptake mass (PNNL-16891, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO₄ Solution Injection and Sr-90 Immobilization in 100-N Sediments*).

1.3.2 Apatite Placement in the Subsurface

Because solid-phase apatite exists as solid mineral apatite particles, it is difficult to displace laterally from an injection point in the subsurface to any significant distance. The surrounding soil tends to filter and block the particles from propagating outward. Various high-energy emplacement techniques exist to essentially force the particles outward by displacing the surrounding media (e.g., jet injection). In contrast, aqueous calcium-citrate-phosphate solutions injected into groundwater form apatite through in situ precipitation reactions between the apatite-forming chemicals. The advantage of injecting aqueous calcium-citrate-phosphate solutions is that the apatite-forming chemicals can migrate away from the injection point before the apatite precipitation occurs, providing the potential to create a larger treatment zone surrounding the point of injection.

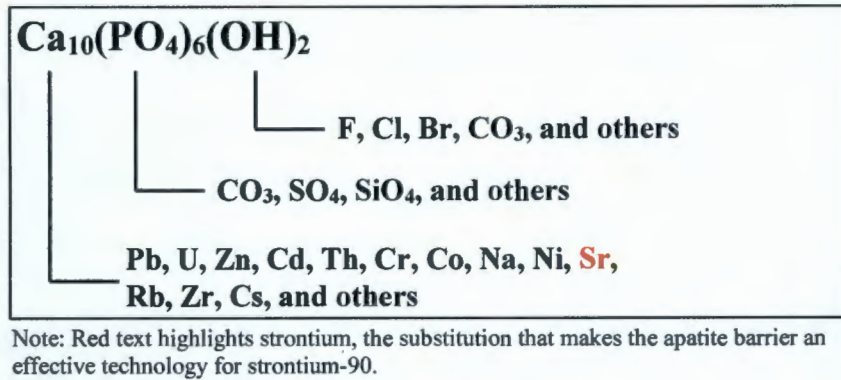


Figure 1-17. Cationic and Anionic Substitutions in Apatite

During treatment of the central (original) 91 m (300 ft) long barrier, a low concentration formulation of the aqueous calcium-citrate-phosphate solution was injected first, followed by a high concentration formulation (Section 1.2.3.3). A phosphate-only formulation was used during the jet injection testing (Section 1.2.3.3). During treatment of the two 91 m (300 ft) upriver and downriver segments of the barrier in 2011, only the high concentration calcium-citrate-phosphate solution was injected. This approach was selected to evaluate the effectiveness of the high concentration formulation without sequential low then high concentration injection, and the transient effect on strontium-90 and other metals released from the soil to the groundwater.

The specific steps of the high concentration calcium-citrate-phosphate injection are as follows:

- Injection of calcium-citrate-phosphate solution and migration of solution from injection point
- Desorption of calcium from sediment by calcium-citrate-phosphate solution (primarily by citrate), thereby reducing the amount of calcium needed in the injection solution (Section 2.5 of PNNL-19572)
- Relatively slow in situ biodegradation of citrate (days) (Section 2.4.2 of PNNL-19572)
- Biodegradation of citrate releases the calcium, which reacts with the phosphate to precipitate apatite and co-precipitate strontium-90 in the treatment zone; amorphous apatite forms within a week and then crystalline apatite forms within a few weeks (Section 2.4.2 of PNNL-19572)
- Adsorption on the apatite surface of strontium-90 migrating with groundwater into the treated zone (minutes) (Section 4.3.2 of PNNL-18303)
- Apatite recrystallization with strontium-90 substitution for calcium (permanent) (months to years) (Section 4.3.2 of PNNL-18303)
- Radioactive decay of strontium-90 to yttrium-90 (half-life of 29.1 years) and of yttrium-90 to zirconium-90 (half-life of 60 hours)

1.3.3 Mass of Apatite Needed for 100-N

Two factors control the amount of apatite needed to sequester strontium-90 at 100-N. One factor, based on mass balance, is the amount of apatite needed to remove sufficient strontium-90 from groundwater over the next 300 years to protect the river. The 300 year timeframe assumes that the initial maximum strontium-90 concentration is 8,000 pCi/L and that 10 half-lives (29.1 years each) of strontium-90 decay are needed to reduce the strontium-90 concentration to below the DWS of 8 pCi/L. The apatite mass

calculation depends on the substitution of strontium for calcium in apatite. If 10 percent substitution is assumed, then 0.96 mg apatite/g sediment (0.54 mg phosphate/g sediment) is sufficient to remove strontium and strontium-90 from the estimated pore volumes of water that will flow through the apatite-laden zone (PNNL-23367, *Hanford Apatite Treatability Test Report Errata: Apatite Mass Loading Calculation*). This calculation assumes an average groundwater flow rate of 0.3 m/day (1 ft/day) and a 9.1 m (30 ft) horizontal width of the apatite barrier, perpendicular to the river.

The 0.96 mg apatite/g sediment would occupy less than 10 percent of the pore space, so a small decrease in permeability within the barrier would be expected (PNNL-23367).

The second factor that controls the amount of apatite needed to sequester sufficient strontium-90 is the relative rates of removal of strontium-90 by the apatite and flux of strontium-90 in groundwater. Sequestration of the strontium-90 is viable only if the natural groundwater flux of strontium-90 through the barrier is slower than the removal rate of strontium-90 by the apatite. If the strontium flux through the barrier is too high, even highly sorbing strontium-90 could advect through the apatite-laden zone more quickly than it is removed. This issue can be resolved by adding additional apatite in the groundwater system (i.e., greater than the amount needed based on the mass balance calculation) to remove strontium-90 at an increased rate. However, experiments indicate that at the apatite content needed from a mass balance perspective (0.96 mg apatite/g sediment), the rate of strontium-90 incorporation into apatite is more rapid than the strontium groundwater flux by a factor of 2 to 200 (PNNL-23367).

The target apatite content (0.96 mg apatite/g sediment) corresponds to one pore volume formulation concentration, on a molar basis, of 51 mM of phosphate precipitated in sediment with no retardation. Assuming a phosphate retardation factor of 2.0 during injections (based on laboratory and field calcium-citrate-phosphate injections), the target apatite content would correspond to a two pore volume concentration of 26 mM phosphate. The high concentration solution was specified at 40 mM phosphate as a result of phosphate solubility limits and other technical considerations, and therefore, includes a safety factor to reach the target phosphate (and apatite) mass loading in the sediment. The target apatite concentration for the saturated zone will be 0.96 mg apatite/g sediment, or less, depending on observed permeability changes.

1.3.4 Formulation of Calcium-Citrate-Phosphate Solution

The formulation of the calcium-citrate-phosphate aqueous solution to be injected into the strontium-90-contaminated aquifer near the Columbia River was based on multiple objectives. First, sufficient mass of phosphate needed to be emplaced in the aquifer to sequester strontium-90 for 300 years, as defined by both mass balance and strontium-90 flux rate considerations (Section 1.3.3). Second, any solution injected into the aquifer that is of higher ionic strength than groundwater will cause some initial desorption of strontium-90 (and Sr^{2+} , Ca^{2+} , and Mg^{2+}) from the sediment, as 99 percent of the strontium-90 mass is adsorbed by ion exchange on sediment minerals (PNNL-17429). The ionic strength of the injecting solution, the concentrations of the monovalent and divalent ions in the solution, and the total volume injected all affect the ion exchange process.

The original concept for field-scale deployment of the apatite PRB technology involved injecting a low concentration, apatite-forming solution, followed by higher concentration injections as required to emplace sufficient treatment capacity to meet remedial objectives. The low concentration injections were designed to provide a small amount of treatment capacity, thus stabilizing the strontium-90 residing within the treatment zone while minimizing strontium-90 mobilization through the injection of high-ionic-strength solutions. However, results from the low concentration field testing and subsequent laboratory studies determined that modifying the solution to a calcium-poor formulation was a better approach for maximizing apatite formation while minimizing short-term increases in strontium-90 concentration. This modified formulation, which relies more heavily on calcium naturally present in the

aquifer sediments as a source for apatite formation, was used during the high concentration treatments conducted in 2008 (PNNL-19572).

The modified high concentration formulation consists of 3.6 mM calcium, 9 mM citrate, and 40 mM phosphate. This solution was identified as the best formulation for meeting the following objectives: minimize the number of injection operations required, minimize short-term increases in strontium-90 and other metal ion concentrations associated with injection of high-ionic-strength solutions, and keep injection formulations well below solubility limits to reduce the potential for operational challenges associated with solution stability. The modified high concentration, calcium-poor, calcium-citrate-phosphate solution uses the existing calcium adsorbed to the Hanford sediments to meet the stoichiometric ratio of calcium to phosphate (5:3) reflected in the apatite structure, and optimizes in situ precipitation (Section 2.5.1 of PNNL-19572).

A detailed discussion of the different injection formulations that have been tested and the development of the high concentration calcium-citrate-phosphate formulation used in the 2011 injections is provided in Section 2.5 of PNNL-19572 and is summarized in Section 2.4 of DOE/RL-2010-29.

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2 Design Optimization Study Approach

The DOS was conducted for further evaluation of the apatite PRB technology. Building on work completed under the original treatability test (DOE/RL-2005-96), the DOS was planned to evaluate potentially improved methods for delivery and emplacement of apatite-forming chemicals on a larger scale. During implementation of the DOS in 2011, the 91 m (300 ft) long apatite PRB installed during the treatability test was extended by 183 m (600 ft) to a length of 274 m (900 ft).

The approach for the DOS was described in DOE/RL-2010-29. Prior to injection of apatite solutions in the barrier network wells under this study, DOE/RL-2010-29 was modified by TPA-CN-474, *Tri-Party Agreement Change Notice Form: Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit, DOE/RL-2010-29, Rev. 0*, which changed and clarified the requirements for sampling and recording field observations and readings. Technical guidance for the injection of the apatite solutions was provided in SGW-47614, *Field Test Instruction 100-NR-2 Operable Unit Design Optimization Study for Sequestration of SR-90 Saturated Zone Apatite Permeable Reactive Barrier Extension*.

2.1 Design Optimization Objectives

Deviations from the design optimization plan that impact evaluation of the objectives in this section are discussed in Section 2.6 of this report. The following objectives of the DOS (Section 3 of DOE/RL-2010-29) are evaluated in Section 3.3 of this report using data and observations from the 2011 injections:

1. Refine application of the high concentration calcium-citrate-phosphate solution over a larger scale.

Refine the application of the high concentration calcium-citrate-phosphate solution through testing the well design, injection equipment, monitoring well sampling, and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions.

2. Test the effectiveness of high concentration calcium-citrate-phosphate injection in previously untested sediment to compare with areas that received sequential injections of low- then high-concentration calcium-citrate-phosphate injections.

The effectiveness will be demonstrated through long-term monitoring of wells and aquifer tubes as explained in Section 6 of the DOS through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking of transient effects of increased metals and anions.

3. Test the new well design installed under DOE/RL-2009-32 to evaluate the adequacy of injection solution delivery to the target zone.

The new well design will be evaluated through monitoring of groundwater and aquifer tubes as described in Section 6 of the DOS through collection of field conductivity measurements in conjunction with groundwater sampling for phosphate.

4. Test and optimize operation of the new injection system to verify that the system can deliver the designed injection solution flow volume at multiple well locations. Determine whether the new well design and injection system can complete chemical injections at various river stages, thereby eliminating the need for injections during specific river levels.

This will be evaluated by performing injections independent of river stage and collecting field conductivity measurements in conjunction with groundwater sampling for phosphate to determine the treatment area achieved.

5. Evaluate that PRB can achieve up to 90 percent reduction in strontium-90 flux to the river.

This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and by tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4 [of the DOS].

6. Further test the impact the high concentration calcium-citrate-phosphate solution has on the release of strontium-90 and other metals from previously untreated sediments to groundwater.

This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4 [of the DOS].

An unstated design objective, based on the approach used to implement the DOS in 2011, was to test the effectiveness of injecting adjacent shallow wells simultaneously and of injecting adjacent deep wells simultaneously.

2.2 Experimental Design

The general experimental design for installation of the injection wells and injection of the apatite solution was provided in Section 4 of DOE/RL-2010-29. The detailed experimental design for injection of the apatite solution and formulation of the apatite solution was provided in Sections 2 and 3 of SGW-47614.

2.2.1 Injection Wells

Between November 2009 and April 2010, 146 injection wells were installed to extend the length of the apatite barrier well network from 91 m (300 ft) to 762 m (2,500 ft). They were spaced 4.6 m (15 ft) apart and constructed using 15.2 cm (6 in.) diameter polyvinyl chloride (PVC) screen and casing. The shallow injection wells that were to target the Hanford formation have 1.5 m (5 ft) long screens from approximately 3.0 to 4.6 m (10 to 15 ft) below ground surface (bgs). The deep injection wells that target the Ringold Formation have 2.1 m (7 ft) long screens from approximately 5.2 to 7.3 m (17 to 24 ft) bgs. Along the length of the barrier extensions, the shallow injection wells alternate with the deep injection wells (Figure 1-7). The range of screen depths from 3.1 to 7.3 m (10 to 24 ft) was based on the strontium-90 vertical profile sampling conducted during installation of the pilot test wells (Section 4.2 of DOE/RL-2010-29). The top of the well casing was just below the ground surface. When not being used for injection, the wells were sealed.

Between November 2009 and April 2010, 25 performance monitoring wells were installed downgradient between the barrier network wells and the river. The performance monitoring wells were constructed using 15.2 cm (6 in.) diameter PVC screen and casing and have 2.1 m (7 ft) long screens from approximately 5.2 to 7.3 m (17 to 24 ft) bgs targeting the Ringold Formation. All of the performance monitoring wells for the extended barrier are screened only in this deeper zone.

During drilling of all the wells, radiological surveys were performed on drill cuttings, geologic samples, temporary drive casing, core barrel, and the driller's control station using standard radiological field screening instruments. Subsurface contamination was detected from ground surface to total depth (0 to approximately 9.1 m [0 to approximately 30 ft] bgs) with contamination levels ranging as high as 33,000 disintegrations per minute (dpm). Contamination above the 5,000 dpm threshold was detected at 31 wells (Section 3.6 of SGW-47791).

All wells were drilled with a minimum 25 cm (10 in.) diameter temporary casing to allow construction of a 15.2 cm (6 in.) diameter resource protection well (i.e., the boreholes were drilled to maintain a minimum 5.1 cm [2 in.] annular space around the permanent well, per WAC 173-160, "Minimum Standards for Construction and Maintenance of Wells"). All of the injection and monitoring wells are

completed flush with ground surface (Figure 2-1). Table 2-1 presents the general construction details for the wells. Well-specific construction details are provided in Table 1 of SGW-47791.



Figure 2-1. Photograph of Some of the Completed Apatite Barrier Injection Wells

Following construction of each well, well development was performed using a low-flow submersible pump to settle the filter pack and to remove fines. The first two wells immediately north (shallow Well 199-N-235 and deep Well 199-N-236) and south (shallow Well 199-N-234 and deep Well 199-N-233) of the existing barrier were limited in the total pumped volume during development to avoid removal of the apatite associated with the barrier. Well development was conducted in all of the other deep wells. Well development was not conducted in any of the other shallow wells because the wells contained only 0 to 0.3 m (0 to 1 ft) of water (Section 3.5 of SGW-47791).

The locations of the injection wells and performance monitoring wells in the 762 m (2,500 ft) long barrier network are shown in Figures 1-12 (upriver) through 1-16 (downriver). The status of the wells is provided in Table 2-2. Figure 1-7 illustrates the alternating shallow and deep barrier well completions, aquifer boundaries, hydrogeology, and radiologically contaminated intervals defined in the boreholes.

All of the 171 wells installed to extend the apatite barrier were sampled following completion. The analytical results for strontium-90, gross beta, the field parameter specific conductivity, total petroleum hydrocarbon-diesel, and nitrate are provided in Table 2-3. All of the analytical and field results are provided in Appendix A.

Table 2-1. General Construction Details for Apatite Barrier Extension Wells

Well Type	Planned Drill Depth m bgs (ft bgs) ^a	Estimated Depth to Water m bgs (ft bgs) ^a	Nominal Screen Length m (ft)	Nominal Screen Placement m bgs (ft bgs)	Nominal Filter Pack Interval m bgs (ft bgs) ^b	Nominal Bentonite Pellet Interval m bgs (ft bgs)	Nominal Bentonite Crumbles Interval m bgs (ft bgs)	Nominal Cement Seal Interval m bgs (ft bgs)
Shallow Injection	4.9 (16)	Dependent on river stage (expected between 2.4 and 5.2 [8 and 17])	1.5 (5)	3.0 to 4.6 (10 to 15)	2.7 to 4.6 (9 to 15)	2.1 to 2.7 (7 to 9)	1.5 to 2.1 (5 to 7)	0 to 1.5 (0 to 5)
Deep Injection	7.6 (25)		2.1 (7)	5.2 to 7.3 (17 to 24)	4.9 to 7.6 (16 to 25)	4.0 to 4.9 (13 to 16)	3.0 to 4.0 (10 to 13)	0 to 3.0 (0 to 10)

Source: DOE/RL-2010-29, *Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit* (Table 1).

Note: All completed wells are 15.2 cm (6 in.) diameter polyvinyl chloride casing and screen. Screened intervals and bentonite seal intervals may vary slightly at individual wells.

a. From DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*.

b. Filter pack interval consists of 6 to 9 mesh Colorado silica sand.

bgs = below ground surface

Table 2-2. Status of Apatite Permeable Reactive Barrier Wells, December 2013

	Total Wells	Monitoring Wells	Injection Wells	Injection Completed	Remain to be Injected
Original Barrier (91 m [300 ft] long)	20	4	16	16	0
Barrier Expansion (extend length by 671 m [2,200 ft])	171	25	146	48	98
Total	191	29	162	64	98

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (µS/cm)	TPH-Diesel (µg/L)	Nitrate (µg/L)
Upriver of Original Barrier							
199-N-200/C7327	IW shallow	06/24/2010	17	26	1,106	2,100 X	1,370 UDX
199-N-201/C7326	IW deep	04/6/2010	16	38	1,155	3,500	24,200 D
199-N-202/C7325	IW shallow	06/24/2010	9.7	61	1,109	3,200 X	54,000 DX
		06/24/2010	12	56		3,100 X	52,700 D
199-N-203/C7324	IW deep	04/06/2010	11	40	1,213	3,600	4,360 D
199-N-204/C7323	IW shallow	06/24/2010	16	51	1,196	3,000 X	53,100 D
199-N-205/C7322	IW deep	04/06/2010	-0.27 U	7.7 U	1,110	3,200	11,900 D
199-N-206/C7321	IW shallow	06/24/2010	39	130	1,552	2,700 X	35,500 D
199-N-207/C7320	IW deep	04/01/2010	-1.1 U	28	928	17 U	41,000 D
199-N-208/C7319	IW shallow	06/24/2010	15	67	518	1,400 X	30,600 D
199-N-209/C7318	IW deep	04/06/2010	4.3	19	1,064	2,200	8,460 D
199-N-210/C7317	IW shallow	06/24/2010	5.6	39	182	70 U	11,300 D
199-N-211/C7316	IW deep	04/01/2010	1.8	16	1,107	17 U	6,200 D
199-N-212/C7315	IW shallow	06/24/2010	4.8	12	215.6	70 U	3,530 D
199-N-213/C7314	IW deep	04/01/2010	1.3 U	12	892	17 U	33,400 D
199-N-214/C7313	IW shallow	06/25/2010	27	56	219	70 U	8,410 D
199-N-215/C7312	IW deep	04/01/2010	3.1	17	1,142	17 U	69,900 D
199-N-216/C7311	IW shallow	06/25/2010	41	99	510	70 U	35,800 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-217/C7310	IW deep	04/01/2010	-0.58 U	17	1,329	17 U	48,700 D
199-N-218/C7309	IW shallow	06/25/2010	110	220	1,421	70 U	156,000 D
199-N-219/C7308	IW deep	04/01/2010	12	40	1,306	17 U	4,470 D
199-N-220/C7307	IW shallow	06/25/2010	91	160	1,606	90 U	32,400
199-N-221/C7306	IW deep	04/01/2010	120	260	881	17 U	51,400 D
199-N-222/C7305	IW shallow	06/25/2010	260	640	2,886	100 U	1,370 UD
199-N-223/C7304	IW deep	04/01/2010	700	1,300	1,023	17 U	92,500 D
199-N-224/C7303	IW shallow	06/25/2010	430	780	511	70 U	83,200 D
199-N-225/C7302	IW deep	03/31/2010	570	1,300	940	70 U	63,700 D
199-N-226/C7301	IW shallow	06/25/2010	170	310	143.3	70 U	1,470 D
199-N-227/C7300	IW deep	03/31/2010	640	1,500	957	70 U	67,300 D
199-N-228/C7299	IW shallow	06/25/2010	160	290	153.9	70 U	4,690 D
199-N-229/C7298	IW deep	03/31/2010	910	1,900	849	70 U	66,400 D
199-N-230/C7297	IW shallow	06/25/2010	290	390	154.9	70 U	5,220 D
199-N-231/C7296	IW deep	03/31/2010	2,100	4,500	733	70 U	55,300 D
199-N-232/C7295	IW shallow	06/25/2010	260	540	164.5	70 U	1,910 D
199-N-233/C7294	IW deep	03/31/2010	1,800	4,400	716	70 U	43,700 D
199-N-234/C7293	IW shallow	06/25/2010	84	250	346	70 U	10,100 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
Downriver of Original Segment							
199-N-235/C7328	IW shallow	06/10/2010	130	300	215.1	NA	5,620 D
199-N-236/C7329	IW deep	07/29/2010	620	1,200	321	NA	16,000 D
199-N-237/C7330	IW shallow	06/10/2010	270	560	208.7	NA	6,770 D
199-N-238/C7331	IW deep	07/29/2010	110	220	155.6	NA	4,130 D
199-N-239/C7332	IW shallow	06/10/2010	140	240	150.5	NA	3,230 D
199-N-240/C7333	IW deep	07/28/2010	330	570	136.1	NA	6,550 D
199-N-241/C7334	IW shallow	06/10/2010	120	120	4162	NA	8,100 D
199-N-242/C7335	IW deep	07/28/2010	230	430	261	NA	19,700 D
199-N-243/C7336	IW shallow	06/10/2010	360	660	306	NA	31,400 D
199-N-244/C7337	IW deep	07/28/2010	460	720	242	NA	18,800 D
199-N-245/C7338	IW shallow	06/10/2010	540	870	320	NA	37,800 D
199-N-246/C7339	IW deep	07/28/2010	480	1,000	297	NA	29,000 D
199-N-247/C7340	IW shallow	06/10/2010	1,800	2,800	435	NA	68,200 D
199-N-248/C7341	IW deep	07/28/2010	1,100	1,900	282	NA	24,700 D
199-N-249/C7342	IW shallow	06/10/2010	590	1,100	227	NA	25,700 D
199-N-250/C7343	IW deep	07/28/2010	900	1,700	283	NA	34,100 D
199-N-251/C7344	IW shallow	06/09/2010	820	1,600	313	NA	37,200 D
199-N-252/C7345	IW deep	07/28/2010	150	300	193.7	NA	12,200 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-253/C7346	IW shallow	06/10/2010	13	34	163.2	NA	8,060 D
199-N-254/C7347	IW deep	07/28/2010	13	31	230	NA	11,200 D
199-N-255/C7348	IW shallow	06/10/2010	39	99	195.6	NA	19,300 D
199-N-256/C7349	IW deep	07/28/2010	56	83	210.2	NA	13,500 D
199-N-257/C7350	IW shallow	06/10/2010	140	410	250	NA	18,300 D
199-N-258/C7351	IW deep	07/28/2010	110	280	194.7	NA	7,660 D
199-N-259/C7352	IW shallow	06/10/2010	220	290	242	NA	25,300 D
199-N-260/C7353	IW deep	08/05/2010	68	140	253	NA	17,500 D
199-N-261/C7354	IW shallow	06/10/2010	44	72	203.5	NA	23,600 D
199-N-262/C7355	IW deep	08/05/2010	9.5	16	277	NA	23,900 D
199-N-263/C7356	IW shallow	06/10/2010	47	92	274	NA	32,400 D
199-N-264/C7357	IW deep	08/05/2010	28	49	255	NA	23,200 D
199-N-265/C7358	IW shallow	06/10/2010	340	620	346	NA	41,100 D
199-N-266/C7359	IW deep	08/05/2010	290	580	238	NA	15,000 D
199-N-267/C7360	IW shallow	06/10/2010	1,400	2,900	337	NA	39,800 D
199-N-268/C7361	IW deep	08/05/2010	1,300	2,700	331	NA	33,500 D
199-N-269/C7362	IW shallow	06/10/2010	1,900	3,900	379	NA	51,800 D
			1,800	3,600	379	NA	51,400 D
199-N-270/C7363	IW deep	08/04/2010	480	1,000	263	NA	21,300 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-271/C7364	IW shallow	06/16/2010	210	430	206.3	NA	13,300 D
199-N-272/C7365	IW deep	08/04/2010	110	220	265	NA	21,800 D
199-N-273/C7366	IW shallow	06/16/2010	670	1,300	190.3	NA	15,100 D
199-N-274/C7367	IW deep	08/04/2010	270	440	204.9	NA	13,000 D
199-N-275/C7368	IW shallow	06/16/2010	340	570	176.9	NA	14,600 D
199-N-276/C7369	IW deep	08/04/2010	200	360	206.6	NA	16,100 D
199-N-277/C7370	IW shallow	06/16/2010	440	660	170.8	NA	6,370 D
199-N-278/C7371	IW deep	08/04/2010	430	840	220	NA	13,300 D
199-N-279/C7372	IW shallow	06/16/2010	1,200	2,300	208.9	NA	16,300 D
199-N-280/C7373	IW deep	08/04/2010	1,800	3,300	286	NA	25,600 D
199-N-281/C7374	IW shallow	06/16/2010	1,300	2,900	235	NA	16,600 D
199-N-282/C7375	IW deep	08/04/2010	2,300	3,800	312	NA	35,700 D
199-N-283/C7376	IW shallow	06/16/2010	290	660	216.9	NA	24,100 D
199-N-284/C7377	IW deep	08/04/2010	210	380	307	NA	32,300 D
199-N-285/C7378	IW shallow	06/16/2010	780	1,700	276	NA	32,700 D
199-N-286/C7379	IW deep	08/04/2010	1,100	2,000	293	NA	28,600 D
199-N-287/C7380	IW shallow	06/16/2010	1,900	3,600	319	NA	35,800 D
199-N-288/C7381	IW deep	08/29/2010	500	1,100	NR	NA	19,500 D
199-N-289/C7382	IW shallow	06/16/2010	650	1,100	195	NA	10,700 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-290/C7383	IW deep	08/29/2010	190	400	NR	NA	34,900 D
199-N-291/C7384	IW shallow	06/16/2010	420	900	157.1	NA	3,680 D
199-N-292/C7385	IW deep	08/29/2010	740	1,800	NR	NA	38,700 D
199-N-293/C7386	IW shallow	06/16/2010	660	1,200	201.8	NA	23,600 D
199-N-294/C7387	IW deep	08/29/2010	1,200	3,000	NR	NA	48,700 D
199-N-295/C7388	IW shallow	06/16/2010	620	1,100	166.6	NA	13,200 D
199-N-296/C7389	IW deep	08/29/2010	810	1,800	NR	NA	3,370 D
199-N-297/C7390	IW shallow	06/16/2010	640	760	194.4	NA	19,100 D
199-N-298/C7391	IW deep	08/29/2010	1,100	2,400	NR	NA	22,500 D
199-N-299/C7392	IW shallow	06/16/2010	920	1,400	172.3	NA	9,520 D
199-N-300/C7393	IW deep	08/29/2010	1,200	2,200	NR	NA	29,500 D
199-N-301/C7394	IW shallow	06/16/2010	720	1,300	224	NA	16,200 D
199-N-302/C7395	IW deep	08/29/2010	280	460	NR	NA	41,600 D
199-N-303/C7396	IW shallow	06/16/2010	150	250	173.7	NA	8,940 D
199-N-304/C7397	IW deep	08/29/2010	37	76	NR	NA	39,000 D
199-N-305/C7398	IW shallow	06/16/2010	320	590	196	NA	6,730 D
			360	600	196	NA	7,970 D
199-N-306/C7399	IW deep	08/29/2010	440	820	NR	NA	43,000 D
199-N-307/C7400	IW shallow	06/21/2010	610	1,200	259	NA	56,700 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-308/C7401	IW deep	08/29/2010	460	870	NR	NA	33,400 D
199-N-309/C7402	IW shallow	06/21/2010	720	1,200	242	NA	52,200 D
199-N-310/C7403	IW deep	08/29/2010	580	1,100	NR	NA	37,600 D
199-N-311/C7404	IW shallow	06/21/2010	350	650	231	NA	24,100 D
199-N-312/C7405	IW deep	08/29/2010	520	1,100	NR	NA	34,400 D
199-N-313/C7406	IW shallow	06/21/2010	400	670	253	NA	27,900 D
199-N-314/C7407	IW deep	08/29/2010	520	1,000	NR	NA	32,400 D
199-N-315/C7408	IW shallow	06/21/2010	380	520	175.6	NA	5,750 D
199-N-316/C7409	IW deep	08/29/2010	140	330	NR	NA	35,100 D
199-N-317/C7410	IW shallow	06/21/2010	110	180	167.7	NA	15,000 D
199-N-318/C7411	IW deep	09/12/2010	420	810	404	NA	42,900 D
199-N-319/C7412	IW shallow	06/21/2010	260	440	172.1	NA	13,500 D
199-N-320/C7413	IW deep	09/12/2010	340	730	429	NA	44,000 D
199-N-321/C7414	IW shallow	06/21/2010	220	450	167.2	NA	7,170 D
199-N-322/C7415	IW deep	09/12/2010	490	1,000	348	NA	30,700 D
199-N-323/C7416	IW shallow	06/21/2010	180	390	164.8	NA	5,490 D
199-N-324/C7417	IW deep	09/12/2010	330	560	372	NA	38,200 D
199-N-325/C7418	IW shallow	06/21/2010	92	210	190.8	NA	19,700 D
199-N-326/C7419	IW deep	09/12/2010	300	510	400	NA	39,300 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-327/C7420	IW shallow	06/21/2010	15	43	195.2	NA	15,900 D
199-N-328/C7421	IW deep	09/12/2010	400	880	407	NA	39,700 D
199-N-329/C7422	IW shallow	06/21/2010	9.9	29	159.5	NA	15,800 D
199-N-330/C7423	IW deep	09/12/2010	450	920	385	NA	39,700 D
199-N-331/C7424	IW shallow	06/21/2010	47	110	187.1	NA	19,700 D
199-N-332/C7425	IW deep	09/12/2010	480	900	354	NA	35,300 D
199-N-333/C7426	IW shallow	06/21/2010	30	84	153	NA	8,630 D
199-N-334/C7427	IW deep	09/12/2010	88	210	302	NA	27,600 D
199-N-335/C7428	IW shallow	06/21/2010	20	22	148.4	NA	5,490 D
199-N-336/C7429	IW deep	09/12/2010	64	100	263	NA	21,200 D
199-N-337/C7430	IW shallow	06/21/2010	3.4	7.2	147.1	NA	3,480 D
199-N-338/C7431	IW deep	09/12/2010	28	70	298	NA	29,100 D
199-N-339/C7432	IW shallow	06/21/2010	4.9	7	226	NA	30,400 D
199-N-340/C7433	IW deep	09/12/2010	10	40	183.1	NA	29,400 D
199-N-341/C7434	IW shallow	06/21/2010	0.74 U	14	168.9	NA	5,890 D
199-N-342/C7435	IW deep	09/12/2010	2	19	321	NA	29,500 D
199-N-343/C7436	IW shallow	06/21/2010	-0.48 U	0.44 U	181.5	NA	20,300 D
199-N-344/C7437	IW deep	09/12/2010	-3.3 U	8.8	329	NA	34,300 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μ S/cm)	TPH-Diesel (μ g/L)	Nitrate (μ g/L)
199-N-345/C7438	IW shallow	06/21/2010	-2.2 U	-0.06 U	187.9	NA	24,400 D
			-1.6 U	1.4 U	187.9	NA	24,300 D
199-N-346/C7442	MW	04/06/2010	1 U	16	1,096	3,700	13,800 D
199-N-347/C7441	MW	04/06/2010	1.1 U	14	910	17 U	46,900 D
199-N-348/C7440	MW	04/06/2010	1,800	4,400	1,993	3,800	27,600 D
199-N-349/C7439	MW	04/06/2010	230	470	934	17 U	74,800 D
			220	520		17 U	73,500 D
199-N-350/C7443	MW	07/29/2010	240	450	156.2	NA	3,620 D
199-N-351/C7444	MW	07/28/2010	350	720	218.4	NA	16,100 D
199-N-352/C7445	MW	07/28/2010	580	1,000	179.7	NA	5,580 D
199-N-353/C7446	MW	07/28/2010	83	170	180.4	NA	6,460 D
199-N-354/C7447	MW	08/05/2010	12	24	242	NA	22,800 D
199-N-355/C7448	MW	08/05/2010	1,400	2,200	277	NA	23,400 D
199-N-356/C7449	MW	08/04/2010	300	550	189.5	NA	11,000 D
199-N-357/C7450	MW	08/04/2010	1,400	2,400	224	NA	14,200 D
			1,300	2,700		NA	14,300 D
199-N-358/C7451	MW	08/04/2010	920	1,400	256	NA	23,300 D
199-N-359/C7452	MW	08/29/2010	210	450	NR	NA	36,700 D
199-N-360/C7453	MW	08/29/2010	700	1,500	NR	NA	13,700 D
199-N-361/C7454	MW	08/29/2010	29	68	NR	NA	32,800 D

Table 2-3. Selected Analytical Results for Wells Installed to Extend Apatite Barrier Length to 762 m (2,500 ft)

Well Name/Well ID	Purpose	Date Sampled	Strontium-90 (pCi/L)	Gross Beta (pCi/L)	Specific Conductivity (μS/cm)	TPH-Diesel (μg/L)	Nitrate (μg/L)
199-N-362/C7455	MW	08/29/2010	450	840	NR	NA	30,900 D
			410	850	NR	NA	30,700 D
199-N-363/C7456	MW	09/12/2010	470	980	418	NA	42,500 D
199-N-364/C7457	MW	09/12/2010	200	460	281	NA	20,500 D
199-N-365/C7458	MW	09/12/2010	180	400	384	NA	36,700 D
199-N-366/C7459	MW	09/12/2010	220	420	304	NA	26,400 D
199-N-367/C7463	MW	09/12/2010	21	48	283	NA	25,000 D
			20	42	283	NA	24,700 D
199-N-368/C7460	MW, Core	07/29/2010	130	320	311	NA	15,400 D
199-N-369/C7461	MW, Core	07/29/2010	200	400	290	NA	13,600 D
			170	420		NA	13,500 D
199-N-370/C7462	MW, Core	07/29/2010	220	520	361	NA	16,800 D

IW = injection well

MW = monitoring well

NA = not analyzed; TPH-diesel analyzed in samples from upriver wells only.

NR = not recorded

TPH = total petroleum hydrocarbon

Core = continuous sediment cores collected to characterize distribution of phosphate mass and strontium-90 as a result of emplacement of original apatite permeable reactive barrier (PNNL-19572, 100-NR-2 Apatite Treatability Test: High-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization Final Report)

D = analyzed using a secondary dilution factor

U = analyzed for but not detected

X = additional notes described in laboratory report

2.2.2 Injection System Design

This section provides a description of the injection system design used in the 2011 injections. The 100-NR-2 OU Apatite Barrier Injection System Design Description is provided in Appendix B and describes the function, design requirements, physical characteristics, operating principles, and design drawing reference list for the injection system. Each apatite injection system consisted of the following equipment:

- A submersible pump placed in the Columbia River to supply water to dilute the two chemical solutions
- Chemical feed tanks located on top of the bluff above the river
- A skid containing equipment for blending the chemical solutions and the river water at carefully controlled ratios and flow rates and injecting the mixed solution into injection wells
- A generator to supply electrical power
- An electrical distribution system
- Interconnecting hoses
- Injection wells

The two chemical mixing and injection skids were similar in that each contained an inlet filter for the river water, an electrical distribution and process control system, flow meters for monitoring water and chemical solution flows, chemical feed pumps, sample points, pressure gauges, pressure regulators, and manual valves. A photo of one of the injection skids is shown on Figure 2-2, and a schematic of the injection system is shown on Figure 2-3.



Figure 2-2. Injection Skid Used During the 2011 Apatite Barrier Well Injections

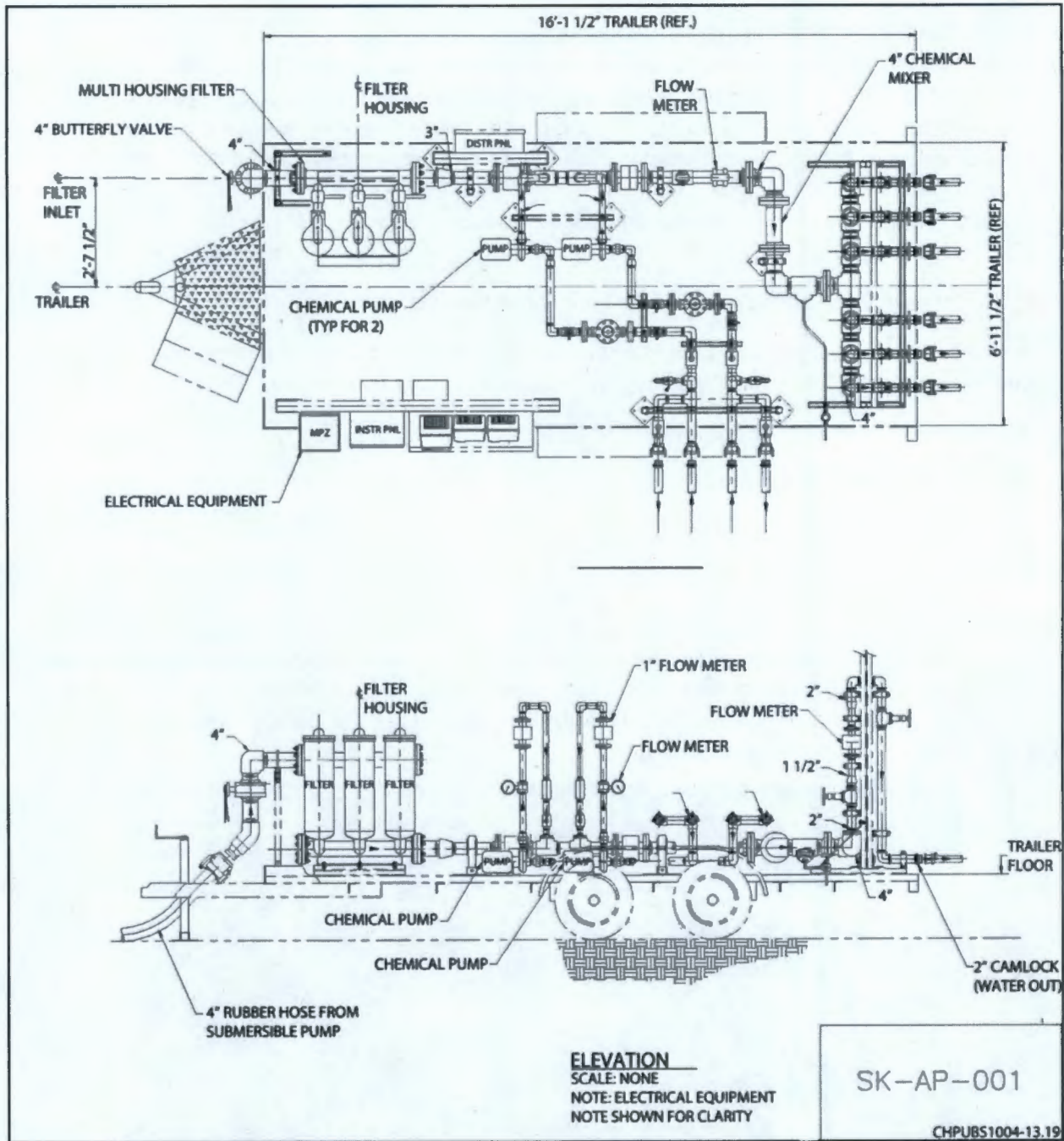


Figure 2-3. Schematic of Injection System Used During the 2011 Apatite Barrier Well Injections

The two chemical solutions (calcium citrate and phosphate) drained from portable storage feed tanks located on the bluff above the injection site through 5.1 cm (2 in.) diameter clear reinforced hoses to the chemical mixing and injection skids located on the shoreline road (the clear hoses at the middle of the skid on Figure 2-4). Water was pumped from the river through a 10.2 cm (4 in.) diameter chemical hose to the skid (the black hose on the left end of the skid in Figure 2-4) where it was filtered and then mixed with the chemical solutions to obtain the correct concentrations for injection. Each skid contained three parallel filters. The filters were sized so that only two needed to be on-line at any given time. This allowed operations to continue during filter changes. Adjustable frequency drives (AFDs) on the river water pumps and chemical solution pumps were set so that the correct ratio of water to chemical solutions was maintained in the mixture. The desired river water flow was set on the river pump AFD. Then the two chemical solution pump AFDs automatically adjusted the chemical solution flows to maintain the correct ratio. The mixed solution flowed from the skids through 5.1 cm (2 in.) diameter hoses to the injection wells (the six black hoses on the right side of the skid in Figure 2-4). A splitter installed on the skids allowed simultaneous injection of the mixed solution into six wells at one time from one skid.

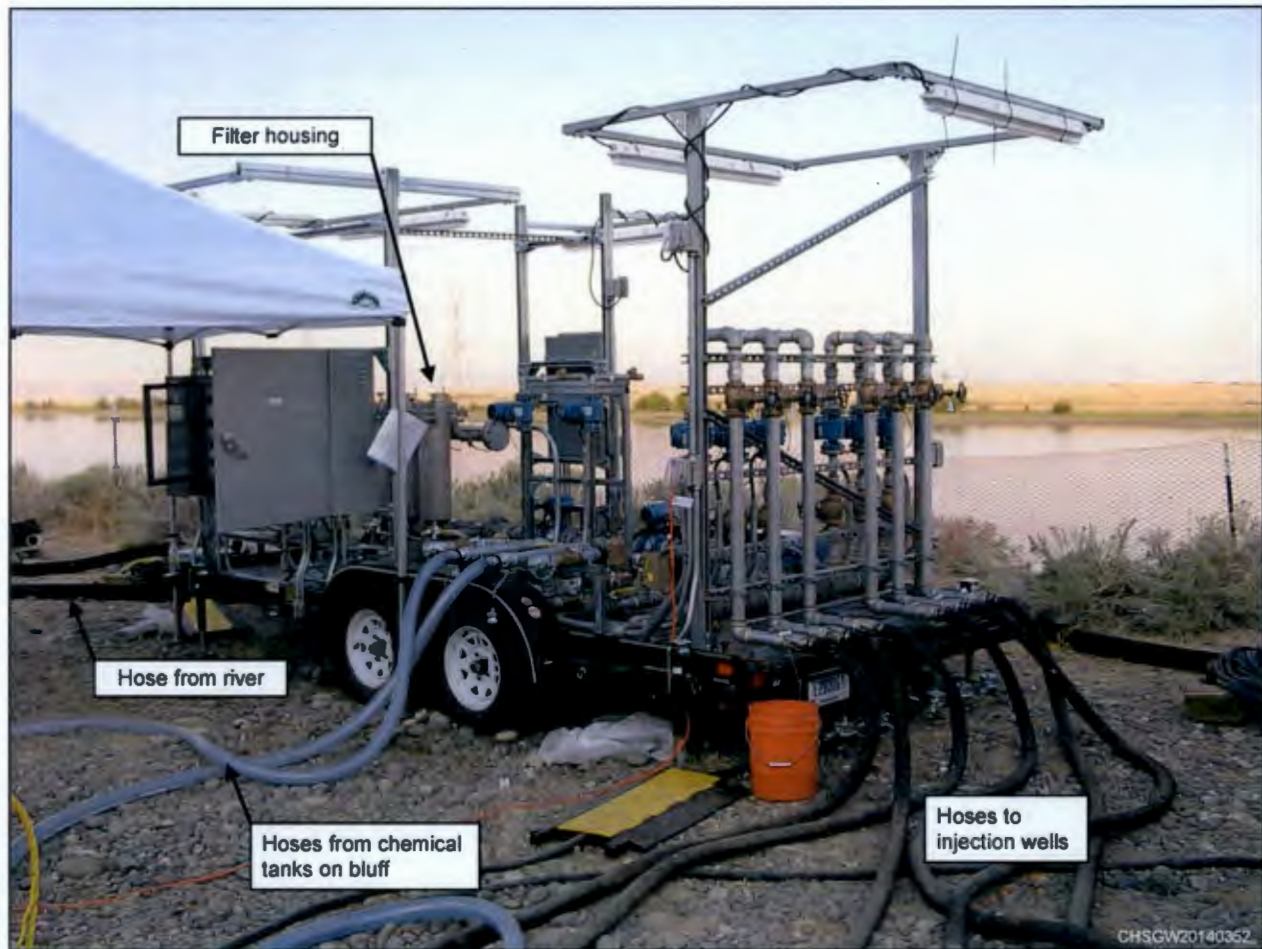


Figure 2-4. Hoses Connected to Injection Skid Used During the 2011 Apatite Barrier Well Injections

The documents prepared to support design of the injection systems are listed in Table 2-4.

Table 2-4. 100-NR-2 Operable Unit Apatite Barrier Injection System Design Documents

Design Documents	
SGW-44606	<i>Apatite Injection Piping Calculation and Model</i>
SGW-48737	<i>Apatite Injection System Civil/Structural Calculations</i>
SGW-48225	<i>Apatite River Pump Skid Analysis</i>

Note: Complete reference citations are provided in Chapter 5.

2.2.2.1 Dilution Water Supply System

Dilution water for the apatite barrier injection system was supplied by a submersible pump located in the Columbia River at a distance of 15.2 to 30.5 m (50 to 100 ft) offshore. The pump was installed in a 20.3 cm (8 in.) diameter Schedule 40 PVC pipe with a fish screen attached to the inlet (Figure 2-5). The fish screen was 25.4 cm (10 in.) diameter by 152.4 cm (60 in.) long, with flow capacity of 946 L/min (250 gal/min). The screen met the 0.06 meters/second (0.2 foot/second) approach velocity criterion of the U.S. Bureau of Reclamation. The pump and screen were mounted on a 0.9 m by 2.4 m (3 ft by 8 ft) angle iron framework covered by a sheet of 0.95 cm (0.375 in.) thick aluminum (Figure 2-6). A swivel hoist ring was attached near the front and rear corners on one side of the framework so the pump assembly could be rigged and lowered into the river from a boat. A 10.2 cm (4 in.) diameter chemical hose was connected to the pump outlet and extended from the pump to the shore to connect the pump to the skid located on the river bank. A submersible power cable was hardwired to the pump motor with the other end connected to the chemical injection skid power panel. Two red buoys were used to mark the location of each submerged pump (Figure 2-7).



Figure 2-5. River Pump with Fish Screen



Figure 2-6. River Pump with Fish Screen Deployment during 2011 Apatite Injections



Figure 2-7. River Pump Hoses and Buoys during 2011 Apatite Injections

2.2.2.2 Chemical Feed System

The apatite forming chemical solutions were delivered to the site by tanker trucks and transferred into vendor-supplied portable feed tanks located on top of the bluff above the Columbia River (Figure 2-8). There were four 28,388 L (7,500 gal) calcium citrate solution feed tanks and eleven 28,388 L (7,500 gal) phosphate solution feed tanks. There was also one 28,388 L (7,500 gal) water tank for flushing equipment. All of the phosphate solution feed tanks were connected to a common manifold. Solution could be fed from individual tanks or from all of the tanks at the same time. All of the phosphate solution needed for an injection was prepared offsite and transferred into the chemical feed tanks prior to the start of the injection. Because the calcium citrate solution was subject to biodegradation, the solution was prepared and delivered to the site during the course of the injection. The four calcium citrate feed tanks were set up as two banks of two tanks each. This allowed chemicals to be fed from one bank of tanks while the other bank was being filled.

The chemical solutions were drained from the tanks to the injection skid by 5.1 cm (2 in.) diameter reinforced clear PVC hoses (Figure 2-9). The hoses consisted of a series of 15.2 m (50 ft) long sections with quick-disconnect fittings on both ends so they could be disassembled and reassembled when the equipment was moved.



Figure 2-8. Array of Chemical Tanks on Bluff above Rivershore



Figure 2-9. Hoses from Chemical Tanks on Bluff above Rivershore to Injection Skid

Each skid contained two chemical feed pumps to control the flow of chemical solutions to the chemical blend system. A pressure control valve was located upstream from each chemical feed pump to limit the pressure to the pump caused by the head of fluid between the chemical tanks and the injection skid. Pressure gauges were located upstream and downstream of the pressure control valves.

Flow indicating transmitters (FITs) were located downstream from the chemical solution feed pumps and had a range of 0 to 114 L/min (0 to 30 gal/min). FITs had a local display and also sent a signal to the corresponding chemical solution pump AFD and to a remote indicator in the control panel (Figure 2-10). These FITs also had a totalizing function that kept track of the total volume.

2.2.2.3 Chemical Blending System

The water from the dilution water feed pump in the river passed through a check valve and then through a filtration system and FIT before it was mixed with the apatite forming chemical solutions.



Figure 2-10. Control Panel on Injection Skid

The filtration system consisted of a bank of three parallel bag filters. The filters had a flow capacity of 833 L/min (220 gal/min) each at a differential pressure of 15.2 kilopascals (kPa) (2.2 psig). The system was operated with two filters online and one offline, which allowed filter element replacement without shutting down the injection operation. The filter housings were 21.9 cm (8.625 in.) outside diameter by 83.8 cm (33 in.) tall carbon steel vessels (Figure 2-4) with pressure gauges installed both upstream and downstream. The filters had upstream and downstream isolation valves as well as vent and drain valves.

FITs were located upstream and downstream from the location where the river water and apatite-forming chemical solutions were combined. The FITs had a range of 0 to 1,136 L/min (0 to 300 gal/minute) and also had a totalizing function. The river water FIT had a local display and also sent a signal to the river pump AFD and to a remote indicator in the control panel (Figure 2-10). The downstream FIT had a local display and also sent a signal to a remote indicator in the control panel. A pressure gauge was located on the combined flow stream.

The static mixer to blend the water and chemical solutions had a capacity of 1,136 L/min (300 gal/min). It had a helical mixing element that directed the flow of material radially toward the pipe walls and back to the center. Additional velocity reversal and flow division resulted from combining alternating right-and left-hand elements, increasing mixing efficiency.

Electrical power for each trailer was supplied by a 480 volt portable generator with a disconnect switch located on a rack adjacent to it. A three phase 480 volt power cord was used to carry power from the

disconnect rack to the skid. The power cord had plugs on both ends to facilitate moving the equipment when needed.

Flow control for the river pump and chemical solution pumps was provided by AFDs. A control panel mounted on the side of the trailer contained FITs for the river water, chemical solutions, and mixed solution (Figure 2-2 and Figure 2-10). It also contained control knobs for adjusting the river water flow set point and the chemical to river water flow ratios. The AFDs were set so that the correct ratio of water to chemical solution was maintained. The river pump AFD controller was adjusted to obtain the desired flow as shown on the river water FIT. The desired chemical to water ratio was set on the chemical pump AFD controllers. The chemical pump AFDs then automatically adjusted the chemical solution flow to maintain the correct ratio when the river water flow was changed.

2.2.2.4 Chemical Injection System

After passing through the static mixer, the diluted chemical mixture solution was split into six streams, which allowed the apatite forming chemical solution to be injected into six wells simultaneously (Figure 2-11). The flow to each well was controlled by a manual globe valve, then the chemical mixture passed through a flow indicating totalizer (FIT) and a block valve and was routed through a 5.1 cm (2 in.) diameter chemical hose to an injection well (Figure 2-12). The hoses were connected to the skid piping and well piping by quick-disconnect fittings.



Figure 2-11. Configuration of Injection Skid where the Diluted Chemical Solution was Split into Six Streams for Simultaneous Injection into Six Wells



Note: The larger diameter hoses (black and white) are the chemical solution delivery lines from the skids to the wells. The smaller diameter white tubes supply air to inflate the downhole well packers.

Figure 2-12. Injection Hoses and Well Packer Inflation Tubes at Injection Wells

FQIs were located downstream from the injection line flow control valves. Each FQI had a range of 0 to 189 L/min (0 to 50 gal/min) and local indication only. A pressure gauge installed between the injection hose and the well head piping provided pressure indication at the well head (Figure 2-13).

The injection well piping was fabricated using 5.1 cm (2 in.) diameter galvanized steel above the landing plate and 5.1 cm (2 in.) diameter PVC below the landing plate (Figure 2-14 and Figure 2-15). The lower 1.5 m (5 ft) of the injection piping was perforated with four rows of 1.3 cm (0.5 in.) diameter holes spaced 15.2 cm (6 in.) apart and was capped at the bottom with a slip-on PVC cap. The injection piping was installed in the wells prior to the start of the injection and was removed when the injection had been completed. The injection piping was fabricated in two lengths: 4.4 m (14.5 ft) for installation in the shallow wells, and 7.5 m (24.5 ft) for installation in the deep wells.



Figure 2-13. Injection Piping Installed at Injection Well

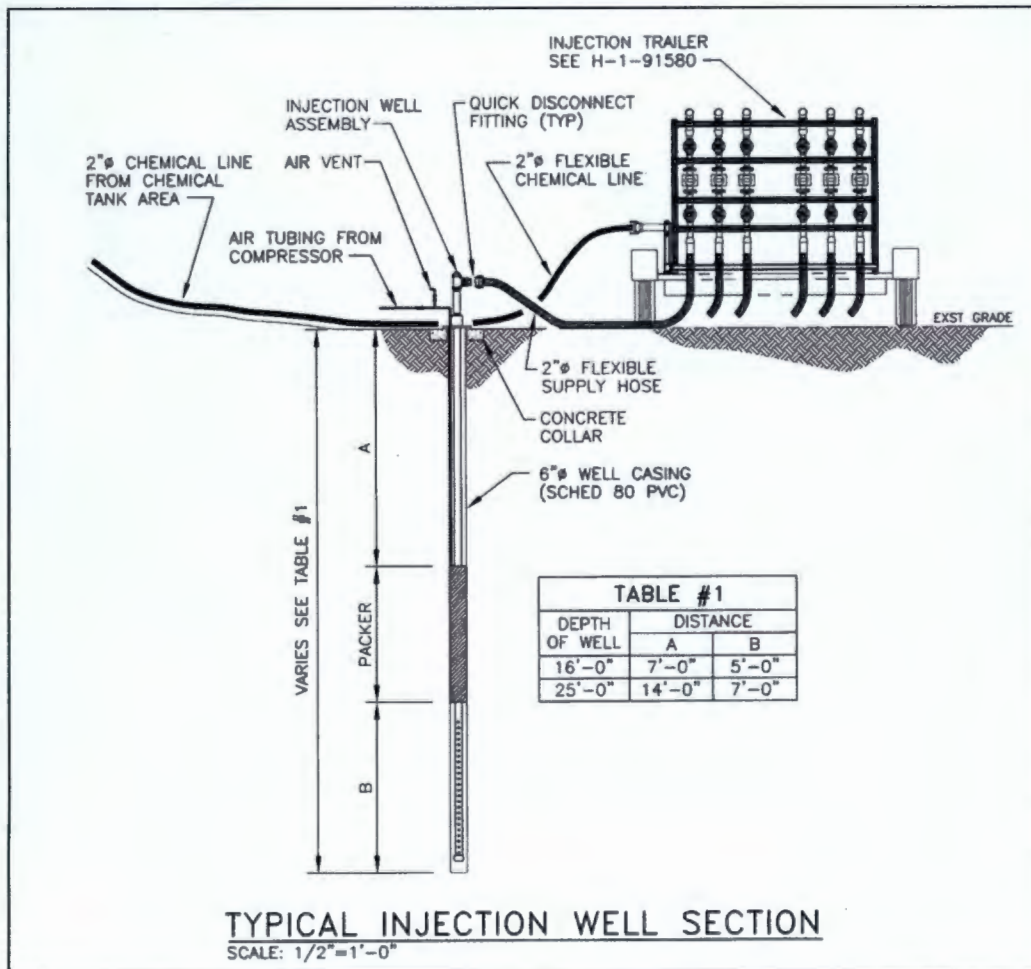


Figure 2-14. Schematic of Injection Well Piping Assembly



Note: The larger galvanized steel pipe above the red landing plate was part of the injection piping. The 0.6 cm (0.25 in.) diameter white tubing supplied air to inflate the packer that is installed in the well. The packer is not visible in the photograph.

Figure 2-15. Injection Well with Packer and Injection Piping Installed

The PVC injection piping was sealed to the steel well piping at ground level with a landing plate (Figure 2-14 and Figure 2-15). The outside of the injection well piping was sealed above the well screen by an inflatable well packer. The packer was inflated with air to seal the annulus between the injection well piping and the well casing. The air was supplied by a portable compressor powered by an electric motor (Figure 2-16). The air was routed to the wells through 0.6 cm (0.25 in.) diameter tubing (Figure 2-15). Isolation and vent valves were located on the line leading to each well packer.



Figure 2-16. Portable Air Compressor used to Supply Air to Inflate Well Packers

2.2.3 Chemical Formulation

The modified high concentration calcium-citrate-phosphate solution was specified in the field test instructions (Section 3.1 of SGW-47614) and used for the 2011 injections. The final calcium: citrate: phosphate ratio was 1:2.5:10 with concentrations of 3.6 mM calcium, 9 mM citrate, and 40 mM phosphate. This formulation was intentionally calcium-deficient compared to the apatite stoichiometric calcium: phosphate ratio of 5:3. This formulation is based on using calcium adsorbed on the aquifer sediments to precipitate as apatite with the injected phosphate. The basis for the high concentration formulation is:

- 9.0 mM trisodium citrate (citrate source at a calcium: citrate ratio of 1:2.5)
- 3.6 mM calcium chloride (calcium source)
- 32.4 mM disodium hydrogenphosphate (phosphate source balanced for pH and solubility)
- 5.6 mM sodium dihydrogenphosphate (phosphate source balanced for pH and solubility)
- 2.0 mM diammonium hydrogenphosphate (nitrate source for citrate biodegradation)

The contract for the offsite preparation and delivery of the chemical mixtures specified food grade chemical solutions with the following concentrations as required in the field test instruction (Section 3.2 of SGW-47614):

- Mix 1: (calcium citrate solution)
 - 108 mM citric acid ($\text{C}_6\text{H}_8\text{O}_7$)
 - 323 mM sodium hydroxide $[\text{NaOH}]$
 - 43.4 mM calcium chloride $[\text{CaCl}_2]$
- Mix 2: (phosphate solution)
 - 456 mM phosphoric acid $[\text{H}_3\text{PO}_4]$
 - 844.8 mM sodium hydroxide $[\text{NaOH}]$
 - 24 mM diammonium hydrogenphosphate $[(\text{NH}_4)_2 \text{HPO}_4]$

The components of the calcium citrate solution and phosphate solution were delivered to the apatite barrier project site in 18,925 L (5,000 gal) tanker trucks. Concentrations of calcium, citrate, and phosphate in the tanker trucks, based on the chemical makeup specification, are provided in Table 2-5.

Table 2-5. Concentrations of Calcium, Citrate, and Phosphate in Tanker Trucks

Chemical	Dry Weight of Chemical (Grams [Pounds])	Volume of Solution (Liters [Gallons])	Concentration (mg/L)
Calcium	91,153.45 (200.96) (CaCl_2)	18,925 (5,000)	1,743
Citrate	392,672.86 (865.70) ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) (citric acid)	18,925 (5,000)	20,455
Phosphate	845,714.02 (1,864.49) (H_3PO_4) (phosphoric acid)	18,925 (5,000)	45,681

The chemical solutions were prepared offsite using deionized water for makeup water applications. This requirement ensured that the makeup water would not contain residual chlorine, or other form of bactericide in the calcium citrate solution that could interfere with biodegradation of the citrate, and calcium (a component of natural groundwater) that could cause precipitates (apatite) to form in the phosphate solution.

2.3 Equipment and Materials

The description of the site utilities, monitoring equipment, analytical equipment, and injection equipment and integration of these components into the operational systems required to conduct the apatite barrier extension is based on Section 5 in DOE/RL-2010-29. Access to the injection construction zone was provided along the existing ramp and gravel access road near the Columbia River. Construction activities were limited by the width of the bench, which in some areas is only 5 m (15 ft).

2.3.1 Site Utilities

Site utility requirements for the apatite injections included a generator and water supply. A diesel generator was used to operate the site facilities, the injection/monitoring equipment, and ancillary equipment. Columbia River water was used to make up the injection solutions.

2.3.2 Injection Equipment

Previous calcium-citrate-phosphate injections were performed using injection skids to mix a dilute solution of river water and concentrated chemicals for injection. The previous injection skids had a limited capacity (injection limited to two wells at a time), which was considered insufficient to implement the larger-scale injections required to expand the barrier by 182.9 m (600 ft). Therefore, two new injection skids were designed and constructed to inject an aqueous mixture of chemical solutions and river water through injection wells to expand the existing 100-NR-2 OU apatite barrier. The new injection skids were designed to increase the coverage area and decrease the time required for each injection. The new injection skids were designed to inject up to six wells simultaneously.

The injection systems are capable of injecting chemical solution at flow rates from 38 to 189 L/min (10 to 50 gal/min) with a total injection capacity for each injection skid of up to 1,136 L/min (300 gal/min), based on a maximum injection rate of 189 L/min (50 gal/min) at a maximum number of 6 wells simultaneously.

2.4 Sampling and Analysis

The sampling and analysis requirements for the samples collected during and after injections are described in Section 7 of SGW-47614. Table 2-6 provides the sampling locations and frequencies from Table 4 in SGW-47614.

Table 2-6. Sampling Locations and Frequencies

Sample Purpose	Sampling Locations	Approximate Sampling Frequency	Analytes ^c
Injection Monitoring	Injection stream	Field parameters every 4 hours, aqueous samples daily	Cations, anions, field parameters
Injection Arrival Monitoring	Specified monitoring locations (see Table 2-7)	Field parameters continuously <i>in situ</i> from wells ^a , aqueous samples at end of each injection campaign (upriver and downriver).	Cations, anions, gross beta, TPH-diesel range ^b , field parameters
Performance Monitoring	Specified monitoring locations (see Table 2-7)	Two and four weeks after end of each injection campaign (upriver and downriver)	Cations, anions, gross beta, TPH-diesel range ^b , field parameters

Source: SGW-47614, *Field Test Instruction 100-NR-2 Operable Unit Design Optimization Study for Sequestration of SR-90 Saturated Zone Apatite Permeable Reactive Barrier Extension* (Table 3 and Table 4).

a. For injection arrival monitoring, probes will be placed in 2 upriver wells during upriver injection and 2 downriver wells during downriver injection. Probes will be placed in 1 upriver and 1 downriver well for performance monitoring.

b. TPH-diesel range organic analysis conducted on samples collected from upriver monitoring wells/aquifer tubes.

c. Major cations/metals: aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cobalt (Co), chromium (Cr; filtered Cr is representative of hexavalent chromium), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), nickel (Ni), zinc (Zn), phosphorus (P), strontium (Sr), sodium (Na), antimony (Sb).

Anions: fluoride (F⁻), chloride (Cl⁻), sulfate (SO₄²⁻), phosphate (PO₄³⁻), nitrite (NO₂⁻), nitrate (NO₃⁻)

TPH-diesel

Gross beta

Field parameters: pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature

The chemical delivery system (skid) was monitored on a regular basis to ensure that appropriate flow rates were maintained. Measurements of system readings (flow rate and pressure) were recorded on an hourly basis, and field parameters (specific conductivity, temperature, pH, and oxidation-reduction potential) were recorded every 4 hours.

Samples of the injection solution were collected from each skid at the start of the injections, mid-way through the injections, and at the end of the injections. The samples were analyzed for anions (by ion chromatography) and major cations (by inductively coupled plasma). One sample of river water was collected at each skid at the start of the injections, prior to mixing with the chemicals.

Injection well flow pressure was recorded hourly at each injection well. The injection flow rate was adjusted as needed to reduce flow pressure so that the downhole packers remained sealed in the injection wells.

Post-injection performance monitoring consisted of the collection of aqueous samples from specified monitoring wells and aquifer tubes after the completion of all upriver injections and after the completion of all downriver injections (Table 2-7). The samples were analyzed for gross beta, anions (by ion chromatography), and major cations and metals (by inductively coupled plasma). Total petroleum hydrocarbon-diesel range organic compound (TPH-diesel) analysis was conducted on samples collected from upriver monitoring wells and aquifer tubes because this area overlaps the petroleum groundwater plume. Field parameters (specific conductivity, temperature, pH, oxidation-reduction potential, and dissolved oxygen) were measured for each sample collected.

Table 2-7. Performance Monitoring Wells and Aquifer Tubes for the 2011 Upriver and Downriver Injections

Injection Number^a	Targeted Zone	Location Relative to Original Barrier	Wells Treated^b		Performance Monitoring Wells^b and Aquifer Tubes
1	Deep Screen	Upriver	C7294, C7298, C7302, C7306, C7310, C7314	N-233, N-229, N-225, N-221, N-217, N-213	N-349 (C7439), N-348 (C7440), N-347 (C7441), N-96A (A9882), N116mArray-1A, N116mArray-2A
2	Deep Screen	Downriver	C7329, C7333, C7337, C7341, C7345, C7349	N-236, N-240, N-244, N-248, N-252, N-256	N-350 (C7443), N-351 (C7444), N-352 (C7445), N-353 (C7446), C7881 ^c , N116mArray-8A
3	Deep Screen	Upriver	C7296, C7300, C7304, C7308, C7312, C7316	N-231, N-227, N-223, N-219, N-215, N-211	N-349 (C7439), N-348 (C7440), N-347 (C7441), N-96A (A9882), N116mArray-1A, N116mArray-2A
4	Deep Screen	Downriver	C7331, C7335, C7339, C7343, C7347, C7351	N-238, N-242, N-246, N-250, N-254, N-258	N-350 (C7443), N-351 (C7444), N-352 (C7445), N-353 (C7446), C7881 ^c , N116mArray-8A

Table 2-7. Performance Monitoring Wells and Aquifer Tubes for the 2011 Upriver and Downriver Injections

Injection Number^a	Targeted Zone	Location Relative to Original Barrier	Wells Treated^b		Performance Monitoring Wells^b and Aquifer Tubes
5	Shallow Screen	Upriver	C7293, C7297, C7301, C7305, C7309, C7313	N-234, N-230, N-226, N-222, N-218, N-214	N-349 (C7439), N-348 (C7440), N-347 (C7441), N-96A (A9882), N116mArray-1A, N116mArray-2A
6	Shallow Screen	Downriver	C7328, C7332, C7336, C7340, C7344, C7348	N-235, N-239, N-243, N-247, N-251, N-255	N-350 (C7443), N-351 (C7444), N-352 (C7445), N-353 (C7446), C7881 ^c , N116mArray-8A
7	Shallow Screen	Upriver	C7295, C7299, C7303, C7307, C7311, C7315	N-232, N-228, N-224, N-220, N-216, N-212	N-349 (C7439), N-348 (C7440), N-347 (C7441), N-96A (A9882), N116mArray-1A, N116mArray-2A
8	Shallow Screen	Downriver	C7330, C7334, C7338, C7342, C7346, C7350	N-237, N-241, N-245, N-249, N-253, N-257	N-350 (C7443), N-351 (C7444), N-352 (C7445), N-353 (C7446), C7881 ^c , N116mArray-8A

Source: Modified from SGW-47614, *Field Test Instruction 100-NR-2 Operable Unit Design Optimization Study for Sequestration of SR-90 Saturated Zone Apatite Permeable Reactive Barrier Extension* (Table 2).

a. As defined in SGW-47614, the injection number does not indicate the order of treatment.

b. Well name prefix "199-" is omitted.

c. Aquifer tube C7881 replaced N116mArray-7A at the 7A location.

2.5 Data Management

All operational, monitoring, and field parameter data were recorded manually on data sheets. Copies of the original data sheets were provided to the 100-N science technical lead for placement into a bound field notebook (controlled by CH2M HILL Plateau Remediation Company). All samples submitted to analytical laboratories were accompanied by the required sampling documentation.

2.6 Deviations from Design Optimization Plan

During the high concentration injections in the original 91 m (300 ft) long barrier wells in 2008, it was concluded that treatment of the shallower Hanford formation is most effective during high river stage and that treatment of the deeper Ringold Formation is most effective at low river stage (PNNL-19572).

Although the field test instruction did not specify a target river stage for the injections, one of the DOS objectives was to determine whether the chemical injections could be completed at various river stages. However, during the DOS, the injections were all performed in September 2011 at approximately the same low river stage.

The field test instruction (Section 6 of SGW-47614) specified continuous in situ monitoring of field parameters (specific conductivity, temperature, pH, oxidation-reduction potential, and dissolved oxygen) at two upriver performance monitoring wells during upriver injections and at two downriver performance

monitoring wells during downriver injections. The in situ probes recorded specific conductivity and temperature in 3 wells (199-N-347, 199-N-349, and 199-N-352) and pH in one well (199-N-347). Data from the fourth well could not be recovered.

The field test instruction (Section 6 of SGW-47614) specified the collection of aqueous samples from downgradient performance monitoring wells and aquifer tubes within approximately 6 hours of the completion of all upriver injections and completion of all downriver injections. The upriver samples were collected 19 hours after completion of injections. The downriver samples were collected 57 hours after completion of injections. At the downriver wells and aquifer tubes, the additional post-injection samples were collected four and five weeks following completion of injections rather than two and four weeks later, as specified in the field instructions.

Although the field test instruction (Section 4 of SGW-47614) provided the flexibility to inject adjacent shallow wells simultaneously and adjacent deep wells simultaneously, the field test instruction noted that injecting every other shallow well or deep well simultaneously would minimize impacts from adjacent injection operations. The inability to monitor barrier network wells adjacent to injection wells made it difficult to evaluate the adequacy of the injection solution delivery to the target zone.

3 Results and Discussion

3.1 Apatite Barrier Emplacement

Injection operations were conducted in 48 wells in September 2011 (Table 3-1): 24 of the wells were upriver of the original 91 m (300 ft) long barrier, and 24 of the wells were downriver of the original barrier. In each group of 24 wells, 12 wells were screened as shallow wells, referred to in the DOS as Hanford formation targeted wells, and 12 wells were screened as deep wells, referred to in the DOS as Ringold Formation targeted wells. As discussed in Section 1.2.2 of this report, the Hanford formation is much shallower in the area of the 100-N shoreline where these 48 wells were screened. As a result, most of the 48 wells were screened in the Ringold Formation. Therefore, these two zones are referred to as the shallow and deep zones in this report.

The configuration of the injection skids and hoses during the injection operations at one of the sites is shown in Figure 3-1.

Table 3-1. Injection Start and Stop Times for High Concentration Barrier Emplacement Operations (September 2011)

Well Name/Well Identification	Target Interval	Start Time		End Time		Duration of Injection (Hrs)
Upriver of Original Barrier						
199-N-211/C7316	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-212/C7315	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-213/C7314	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-214/C7313	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-215/C7312	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-216/C7311	shallow	09/13/2011	09:25	09/15/2011	11:25	50.0
199-N-217/C7310	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-218/C7309	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-219/C7308	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-220/C7307	shallow	09/13/2011	09:25	09/15/2011	11:25	50.0
199-N-221/C7306	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-222/C7305	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-223/C7304	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-224/C7303	shallow	09/13/2011	09:25	09/15/2011	11:25	50.0
199-N-225/C7302	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-226/C7301	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-227/C7300	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-228/C7299	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0

Table 3-1. Injection Start and Stop Times for High Concentration Barrier Emplacement Operations (September 2011)

Well Name/Well Identification	Target Interval	Start Time		End Time		Duration of Injection (Hrs)
199-N-229/C7298	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-230/C7297	shallow	09/13/2011	09:25	09/15/2011	12:25	51.0
199-N-231/C7296	deep	09/07/2011	13:30	09/09/2011	13:00	47.5
199-N-232/C7295	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
199-N-233/C7294	deep	09/07/2011	17:20	09/09/2011	13:00	43.7
199-N-234/C7293	shallow	09/13/2011	09:25	09/15/2011	14:25	53.0
Downriver of Original Barrier						
199-N-235/C7328 (a)	shallow	09/15/2011	12:25	09/15/2011	14:25	2.0
199-N-235/C7328	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-236/C7329 (a)	deep	09/15/2011	11:25	09/15/2011	14:25	3.0
199-N-236/C7329	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-237/C7330 (a)	shallow	09/15/2011	11:25	09/15/2011	14:25	3.0
199-N-237/C7330	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-238/C7331 (a)	deep	09/15/2011	11:25	09/15/2011	14:25	3.0
199-N-238/C7331	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-239/C7332	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-240/C7333	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-241/C7334	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-242/C7335	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-243/C7336	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-244/C7337	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-245/C7338	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-246/C7339	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-247/C7340	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-248/C7341	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-249/C7342	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-250/C7343	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-251/C7344	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5

Table 3-1. Injection Start and Stop Times for High Concentration Barrier Emplacement Operations (September 2011)

Well Name/Well Identification	Target Interval	Start Time		End Time		Duration of Injection (Hrs)
199-N-252/C7345	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-253/C7346	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-254/C7347	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-255/C7348	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-256/C7349	deep	09/21/2011	13:30	09/23/2011	08:00	42.5
199-N-257/C7350	shallow	09/23/2011	10:30	09/25/2011	02:00	39.5
199-N-258/C7351	deep	09/21/2011	13:30	09/23/2011	08:00	42.5

Note: Downriver Wells 199-N-235, 199-N-236, 199-N-237, and 199-N-238 were each used for injection for two or three hours at the end of the upriver shallow injection phase.

3.1.1 Injection Logistics

All 12 of the deep upriver wells were injected from September 7 through September 9 (injection numbers 1 and 3 on Table 2-7), and all 12 of the shallow upriver wells were injected from September 13 through September 15 (injection numbers 5 and 7 on Table 2-7). All 12 of the deep downriver wells were injected from September 21 through September 23 (injection numbers 2 and 4 on Table 2-7), and all 12 of the shallow downriver wells were injected from September 23 through September 25 (injection numbers 6 and 8 on Table 2-7). Two injection skids, each with the capacity to inject six wells simultaneously, were used during each injection period.

All of the upriver injections were completed before the downriver injections to minimize remobilization of the injection equipment between the upriver and downriver locations. Both skids were operated simultaneously in each area (upriver, then downriver) to consolidate operations in one place and to optimize operational time.

Injection operations continued around the clock during each injection period. Injections continued until the total volume of chemical solution had been discharged from the skid to the set of six online wells (nominally 227,000 L [60,000 gal] total per well times 6 wells, for 1,363,000 L [360,000 gal] total per skid).



Figure 3-1. Configuration of Injection Skids and Hoses at One Site during the 2011 Apatite Barrier Well Injections

Workers were on site throughout each injection period to monitor operations. As required, the flow rates of river water, calcium-citrate solution, phosphate solution, and total injection solution were recorded hourly, as were the pressures at the injection wells. Indicator parameters pH, temperature, conductivity, and oxidation-reduction potential of the injection solution were measured and recorded every four hours (Appendix C). Samples of the injection solution were collected at the beginning, middle, and end of injection operations for laboratory analysis (Appendix D).

3.1.2 Groundwater Elevations during Injections

All of the injections were conducted during relatively low river water stage conditions, as indicated by the relatively low ambient groundwater elevations measured at Well 199-N-146 (Figure 3-2, Table 3-2). The minimum river stage elevation for high river conditions is 119 m, and the maximum river stage elevation for low river conditions is 118 m (Section 5.1 of PNNL-19572). The groundwater elevation typically varied by 0.8 to 0.9 m during the upriver injection plus reaction periods and by 0.7 m during the downriver injection plus reaction periods (Table 3-2). The observations in this section of the report are based on the ambient groundwater elevations and the injection well screen elevations (Appendix E).

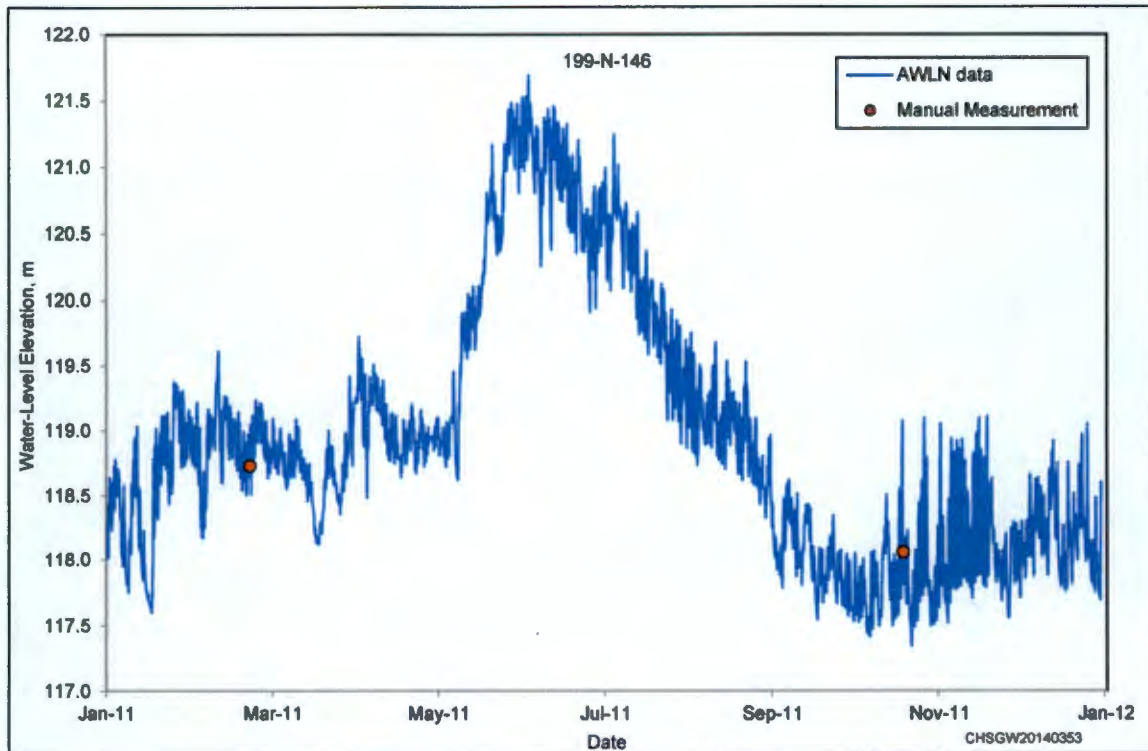


Figure 3-2a. Automated Water Level Data for Well 199-N-146, 2011

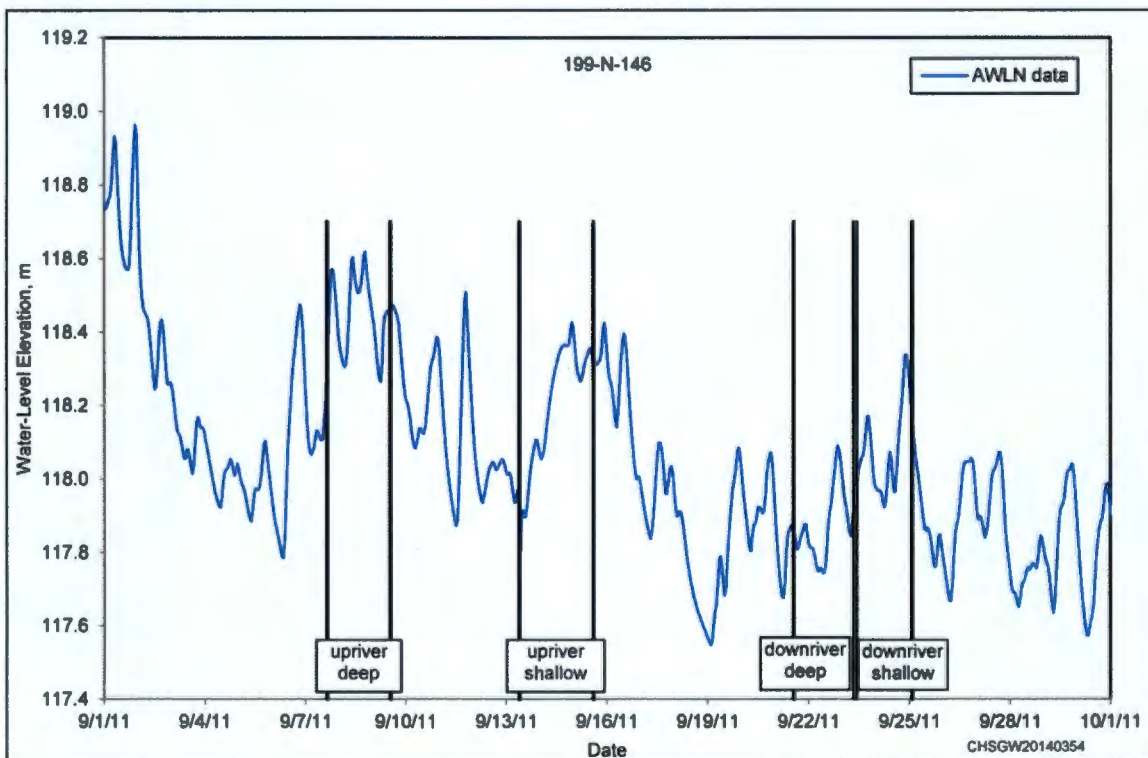


Figure 3-2b. Automated Water Level Data for Well 199-N-146 during Apatite Barrier Well Injections, September 2011

The injections caused temporary increases in the water table elevation in nearby injection and performance monitoring wells. Details regarding water level mounding elevations relative to the well screen elevations are provided in Section 3.1.5 of this report.

Table 3-2. Water Level Elevations during 2011 Apatite Barrier Well Injections based on Well 199-N-146 Automated Water Level Monitoring

Injection Phase	Elevation of Screen Top (m)	Elevation of Screen Bottom (m)	Injection Period Water Level Elevation (m)			Injection + 7-Day Reaction Period Water Level Elevation (m)		
	Average	Average	Average	Maximum	Minimum	Average	Maximum	Minimum
Upriver Deep	117.9	115.8	118.4	118.6	118.2	118.2	118.6	117.8
Upriver Shallow	120.3	118.8	118.2	118.4	117.8	118.0	118.4	117.5
Downriver Deep	116.8	114.7	117.9	118.1	117.7	117.9	118.3	117.6
Downriver Shallow	119.1	117.6	118.1	118.3	117.9	117.9	118.3	117.6

During the upriver injections into the shallow zone, and for the 7-day reaction period following, ambient groundwater elevations remained below the bottom of the shallow injection screens (Table 3-2). As a result, apatite formation would be expected in the shallow zone only if the injections maintained adequately elevated water levels (mounding) and the apatite-forming solutions remained within that interval for the 7-day reaction period.

During the upriver injections into the deep zone, and for the 7-day reaction period following, ambient groundwater elevations remained above the top of the deep injection screen, with a few exceptions (Table 3-2). As a result, apatite formation would be expected within the full thickness of the deep zone from these injections. (The only exception during the injection period was Well 199-N-211, where the minimum water level elevation was 0.11 m below the top of the deep injection screen. The exceptions during the 7-day reaction period were Wells 199-N-211, 199-N-213, 199-N-215, 199-N-225, and 199-N-229, where the minimum water level elevations were below the tops of the deep injection screens by as much as 0.46 m.)

During the downriver injections into the shallow zone, and for the 7-day reaction period following, groundwater elevations remained within the shallow screened zone (Table 3-2). As a result, apatite formation would be expected in the upper part of the shallow zone only if the injections maintained adequately elevated water levels (mounding) and the apatite-forming solutions remained within that interval for the 7-day reaction period.

During the downriver injections into the deep zone, and for the 7-day reaction period following, groundwater elevations remained above the top of the deep screen (Table 3-2). As a result, apatite formation would be expected within the full thickness of the deep zone from these injections.

Well 199-N-146, where the water level data used in this report were measured, is between the original barrier segment and the river. The N-River Gauge was removed in 2010 to facilitate decontamination and

demolition work; therefore, no river gauge was available during the 2011 field work. Comparison of the automated water level monitoring data for Well 199-N-146 and the N River Gauge from 2006 to 2010 indicates that data from Well 199-N-146 can be used as a surrogate for the relative river stage (Figure 3-3).

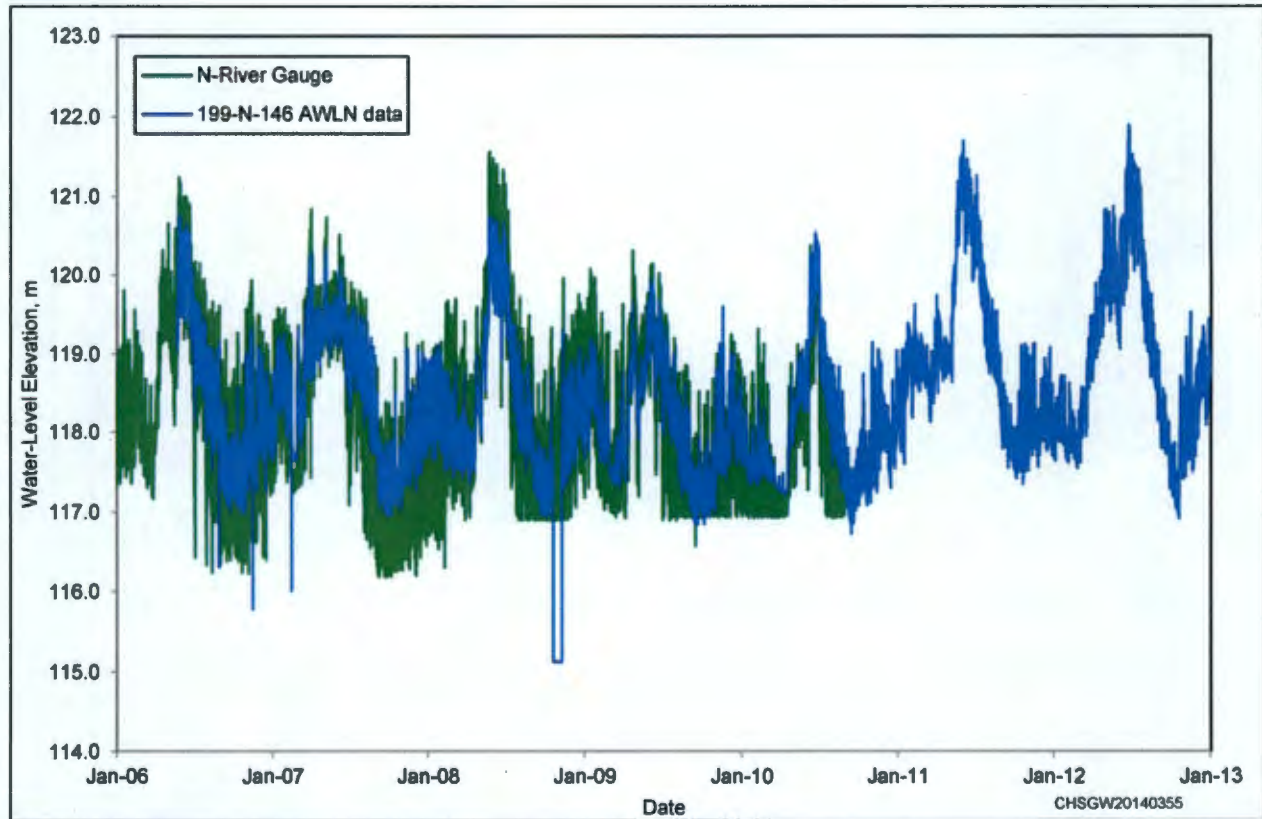


Figure 3-3. Comparison of N-River Gauge Data and Automated Water Level Data for Well 199-N-146 (2006 to 2012)

The water levels in two of the three nearest monitoring wells in the 100-N automated water level monitoring network temporarily increased as a result of the injections (Figure 3-4). Well 199-N-146 is more than 29 m (95 ft) from the closest 2011 upriver injection well and located near the upriver end of the original 90.1 m (300 ft) long barrier segment (Figure 1-13); Well 199-N-147 is near the downriver end of the original barrier segment and is more than 10 m (35 ft) upriver from the nearest 2011 downriver injection well (Figure 1-13); and Well 199-N-99A is more than 132 m (433 ft) downriver of the nearest downriver 2011 injection well (Figure 1-15). Several observations can be made from the water level responses in these monitoring wells during the injections (Figure 3-4):

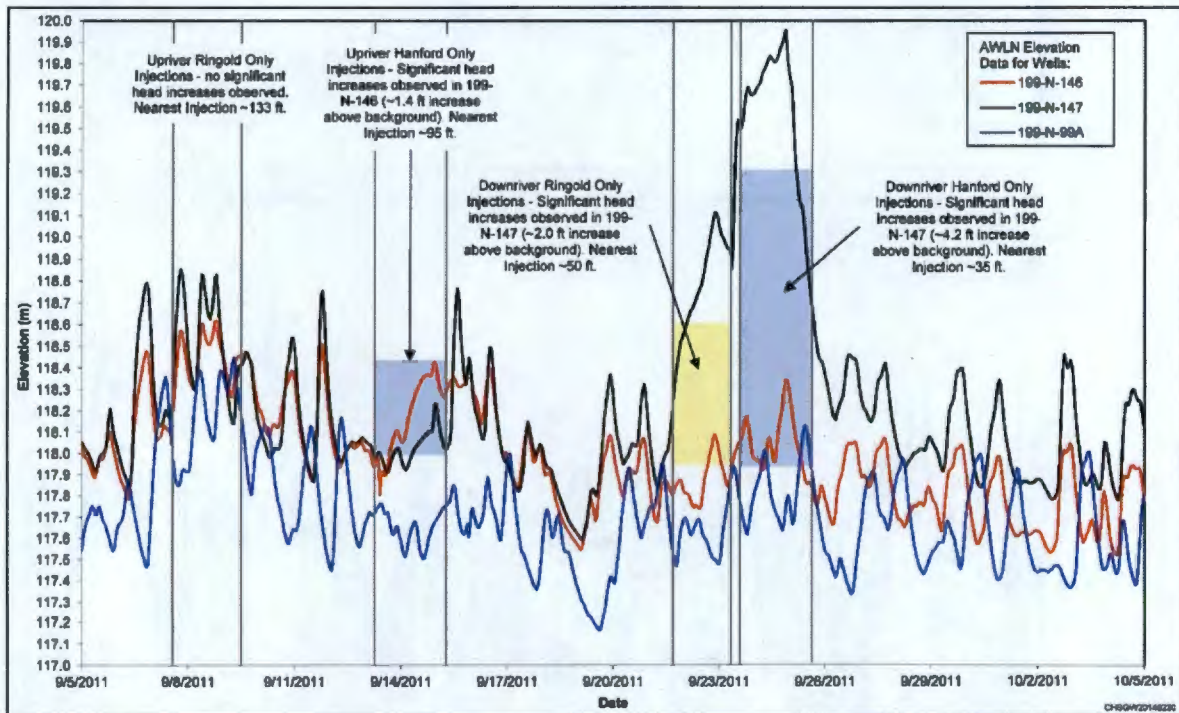


Figure 3-4. Impact of Injections on Water Levels in Wells 199-N-146, 199-N-147, and 199-N-99A

1. There is no apparent change in water level in Well 199-N-99A during either the deep or shallow upriver and downriver injections. This is expected because Well 199-N-99A is far enough away from the 2011 injection wells that no impact is probable.
2. A very slight increase in water level of approximately 0.4 m (1.4 ft) occurred in Well 199-N-146 in response to upriver injections, but only during the shallow injection period (Figure 3-4). This response probably was the result of local mounding created by injections in the shallow wells. Mounding extended downgradient to Well 199-N-146, which is screened across the water table over a large interval that includes both the Hanford and Ringold formations. Increases in water levels were not observed during injection into the deep upriver wells which were slightly further away. These responses were interpreted by comparing changes in water level trends between the three automated water level network wells (Wells 199-N-146, 199-N-147, and 199-N-99A). All three wells trend consistently and more or less similarly when there is no outside influence on the wells except the Columbia River, but the two wells closer to the injected wells show measureable changes during the injections. (As discussed in Section 3.1.5, the increases in water level in performance monitoring Well 199-N-349, located only 4.6 m (15 ft) downgradient from the nearest 2011 upriver injection wells, was much greater during both the shallow and deep injections to the upriver network.)
3. Increases in the water level in Well 199-N-147 were recorded during both the shallow and deep injections in the downriver wells. The increases in Well 199-N-147, which is screened across the water table over an interval that includes both the Hanford and Ringold formations, were higher during injection into the shallow zone wells. The increases probably were the result of local mounding created by the injections. (As discussed in Section 3.1.5, increases in water levels also were recorded in performance monitoring Well 199-N-352, located only 3.3 m (11 ft) downgradient from the nearest 2011 downriver injection wells.)

3.1.3 Volumes of High Concentration Calcium-Citrate-Phosphate Solution Injected

The volume of apatite-forming solution injected in 2011 was measured during operations using the following three methods:

1. **Hourly Flow Rates**—The flow rates on the flow meters for the calcium-citrate solution, phosphate solution, river water, and combined (mixed) solution were recorded hourly during the injections by on-site workers. The hourly flow rate data can be used to calculate the volumes injected during each injection phase, but do not indicate how much solution was received by each individual injection well. These data are referred to as the “hourly flow rate readings” in this report.
2. **Flow Totalizers for Apatite-Forming Chemicals**—The volumes of apatite-forming solutions injected during each injection phase in 2011 were recorded using the flow totalizers built into the injection skids (Figure 2-10). Flow totalizers were included for the calcium-citrate solution feed, the phosphate solution feed, the river water feed, and the combined (mixed) solution feed. The totalizer readings were recorded at the beginning and end of each injection phase (i.e., deep upriver, shallow upriver, deep downriver, shallow downriver) by onsite workers. These flow totalizers for the apatite-forming chemicals are referred to as the “skid totalizers” in this report.
3. **Flow Totalizers for Injection Wells**—Flow totalizers were included for each of the pipes feeding the hoses that connected to the online injection wells (Figure 2-11). The totalizer readings were recorded at the beginning and end of each injection phase by onsite workers. These flow totalizers are referred to as the “well totalizers” in this report.

The hourly flow rate readings, skid totalizer data, and well totalizer data were recorded on the skid monitoring data sheet from the apatite injection technical procedure and on the skid monitoring data sheet from the field test instruction (SGW-47614). The data sheets occasionally differed in the recorded values. The data on both sets of skid monitoring data sheets were evaluated. In cases of differences, the data judged more likely to be correct were used in this report. The data sheets are included in Appendix C of this report.

3.1.3.1 Target Volumes

Based on chemical arrival responses observed during previous barrier treatment operations and injection analysis and design, an injection volume between 227,000 L (60,000 gal) and 454,000 L (120,000 gal) was specified for each well (Section 2 of SGW-47614). In 2011, the target volume per well was 227,000 L (60,000 gal) (based on approximately 1,363,000 L [360,000 gal]) injected per skid for shallow wells and for deep wells).

3.1.3.2 Injected Volumes

The volumes of apatite-forming solution injected during 2011 are summarized for each well in Table 3-3, based on the well totalizer data. In this report, the volume of solution received by each injection well is based on the well totalizer data. In this report, the volume of solution injected by each skid is based on the hourly flow rate readings. The volumes injected in the upriver and downriver wells are shown in Figure 3-5.

Based on the hourly flow rate readings, the total volume of apatite-forming solution injected by the skids in 2011 to upriver wells was 6,004,403 L (1,586,368 gal), and to downriver wells was 5,518,432 L (1,457,974 gal). Injection continued from each skid until the entire volume of solution delivered to the skid had been injected. Downriver Wells 199-N-235, 199-N-236, 199-N-237, and 199-N-238 were each used for injection for two or three hours at the end of the upriver shallow injection period; the downriver total volume includes this volume.

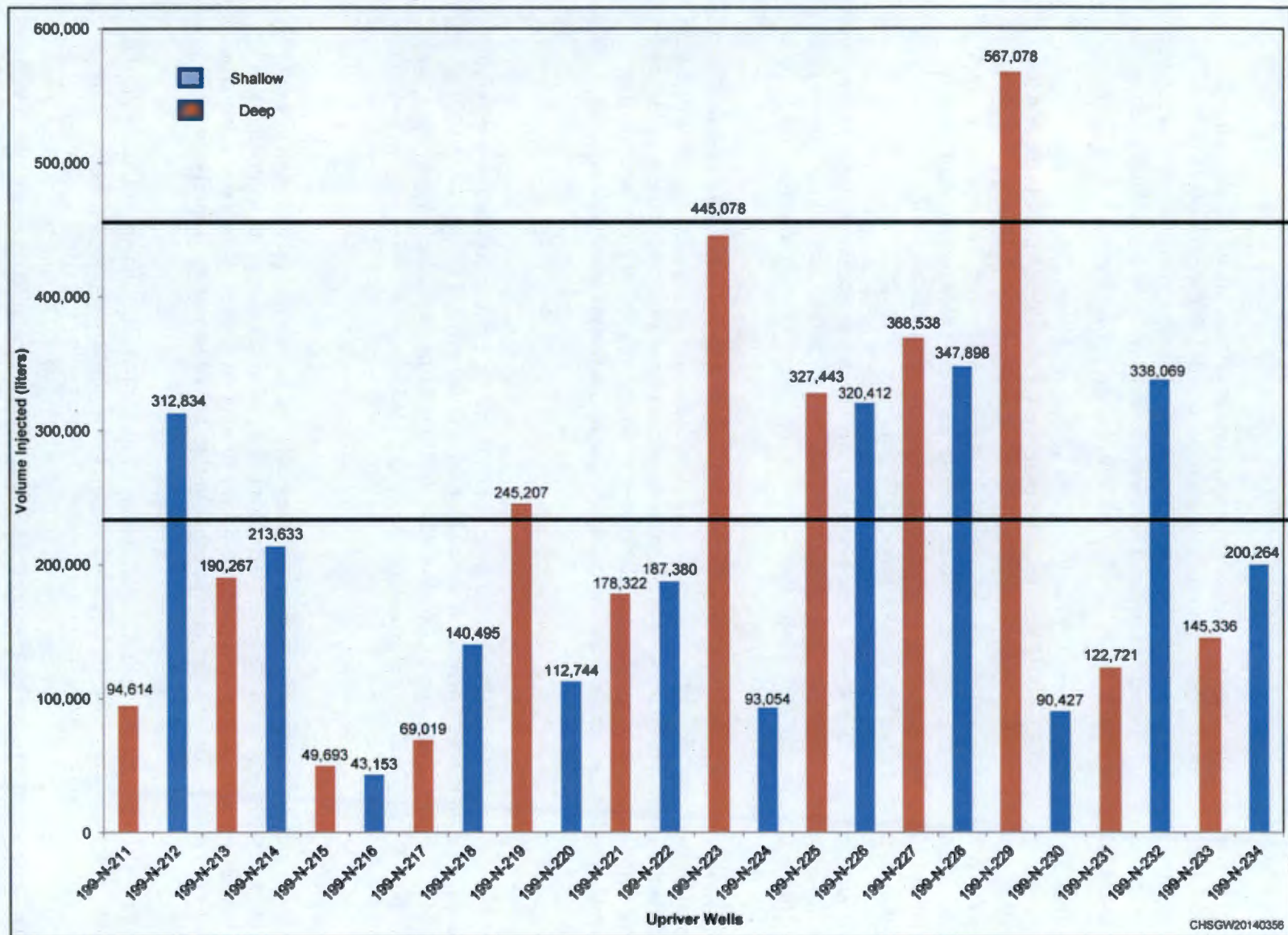


Figure 3-5a. Volumes Injected in Upriver Wells in 2011

3-10

1

2

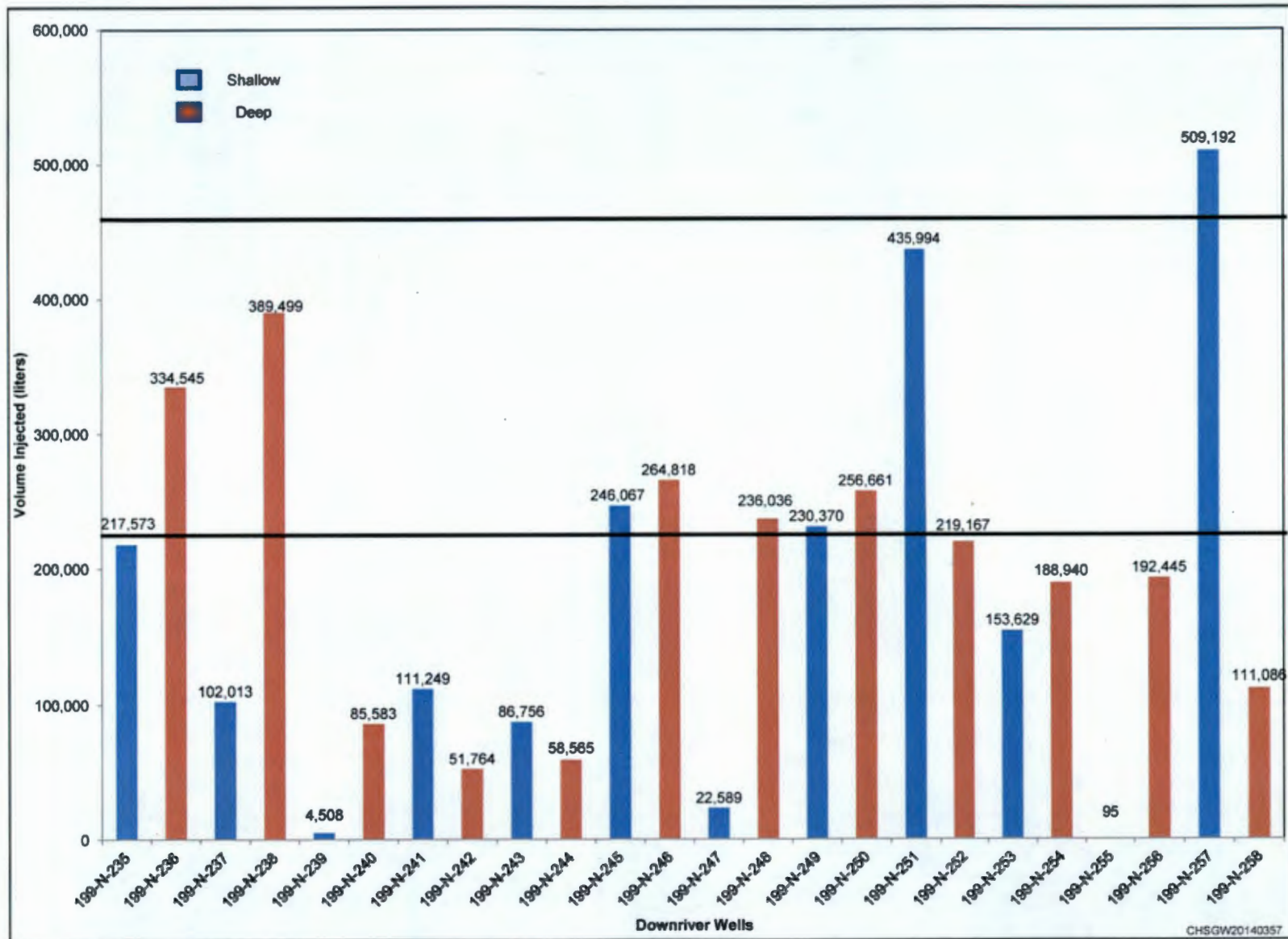


Figure 3-5b. Volumes Injected in Downriver Wells in 2011

Based on the well totalizer data, the volume of solution received by individual upriver wells ranged from 43,153 L (11,401 gal) to 567,076 L (149,822 gal), and the volume of solution received by individual downriver wells ranged from 95 L (25 gal) to 509,192 L (134,529 gal). Based on the well totalizer data, 30 of the 48 injection wells (63 percent) did not receive 227,000 L (60,000 gal) of solution, and 2 wells received more than 454,000 L (120,000 gal).

The volume of solution received by the wells from each skid (i.e., the sum of the volumes recorded by the six well totalizers for each skid) does not equal the volume of solution injected by the skids based on the hourly flow rate readings. In most cases, the volume of solution received by the wells is less than the volume of solution injected based on the hourly flow readings. The volumes differ by up to 39 percent (Table 3-4). The largest discrepancies are associated with skid 2. Volumes that differ by more than 25 percent suggest that one or more of the well totalizers may have malfunctioned. If so, it is possible that some wells may have received more solution than indicated by the well totalizers. Data are not available to distribute the "missing" volume of solution to individual injection wells.

3.1.3.3 Injection Rates

An initial injection rate of 152 L/min (40 gal/min) was specified for injection at each well (Section 2 of SGW-47614). The average injection rate at each well was calculated based on the injection volumes from the well totalizers (Table 3-3) and the injection durations (Table 3-1). Among the 16 wells that received an injection volume between 227,000 L (60,000 gal) and 454,000 L (120,000 gal), average injection rates ranged from 86 L/min (23 gal/min) to 184 L/min (49 gal/min), with a mean of 116 L/min (31 gal/min) (Table 3-3).

3.1.3.4 Injection Solution Concentrations

Samples of the injection mixture of calcium-citrate solution, phosphate solution, and river water were collected from each skid at the start of injections, mid-way through injections, and at the end of injections. A sample of river water also was collected at each skid at the start of injections. The samples were analyzed by a laboratory. A summary of the analytical results for calcium and phosphate is provided in Table 3-5. Although the citrate concentration was not analyzed in the samples, the average concentration in the mixture was calculated using the average calcium concentrations in the samples of the mixture. All of the results are provided in Appendix D.

Based on the hourly flow rate readings for calcium-citrate, phosphate, and river water, the percent of each of these components in the mixed injection fluid was calculated for each skid over the entire injection phase (Tables C-5 through C-8 in Appendix C). During the 2011 injections, the percent of calcium citrate in the mixture ranged from 8.2 to 8.4; the percent of phosphate in the mixture ranged from 8.1 to 8.5; and the percent of river water in the mixture ranged from 83.1 to 83.6. These percentages are consistent with the specified 1:1:10 dilution ratio.

The percentages of calcium-citrate and phosphate chemical components in the solution mixtures for each skid, and the well totalizer volumes, were used to calculate the volume of each chemical component injected into each well. The results are summarized in Appendix C (Tables C-5 through C-8).

3.1.3.5 Mass Injected

The average concentrations of calcium, citrate, and phosphate in the samples of the injection mixtures (Table 3-5) and the well totalizer readings for the volume of the mixture injected into each well (Table 3-3) were used to calculate the masses of calcium, citrate, and phosphate injected into each well (Table 3-6). The concentrations of calcium, citrate, and phosphate in the chemical makeup solutions (Table 2-5) and the volumes of each chemical component injected into each well (Tables C-5 through C-8 in Appendix C) also were used to calculate the masses of calcium, citrate, and phosphate injected into

each well. Results of these two approaches for calculating the masses of calcium, citrate, and phosphate injected are consistent (Tables C-5 through C-8 in Appendix C).

The phosphate injected at each well (based on the average concentration in the injection mixture [Table 3-5]) was used to calculate the apatite formed at each well. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg (Appendix F). Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment.

Results of the injection calculations are presented in Appendix F for each skid during the four injection cycles. The calculations show that the calcium, citrate, and phosphate concentration of the mix injected into each well met the high concentration formulation targets of 3.6 mM, 9 mM, and 40 mM, respectively. Of the 48 wells injected, 10 (or 21 percent) of the wells received less than 80 percent of the target phosphate mass for the target 0.544 mg phosphate/g sediment concentration, and 16 (or 33 percent) of the wells received less than the full target phosphate mass. The wells receiving less than the target phosphate mass are identified with red highlighted text in Table 3-6.

The concentration of apatite formation is calculated based on the mass of phosphate injected into each well. The effective period of barrier performance is also calculated based on the apatite concentration. There are 6 wells where the calculated period of performance would be less than 150 years compared to the 300 year expected performance period. This assumes adequate lateral distribution of the chemical solutions injected into the aquifer matrix. Measurements from monitoring wells downgradient from the injected wells indicate that phosphate reached the monitoring wells. However, measurements/samples in wells adjacent to the injected wells were not taken, so information is not available for full assessment of adequate lateral coverage. Heterogeneities within the aquifer sediments, as noted by very high injection pressures in the relative low permeability wells and higher volumes injected in relatively high permeability wells, may have resulted in areas with a lot of apatite close to the injection well, but with thin treatment areas leading to inadequate lateral coverage and gaps within the barrier with insufficient apatite. This could lead to early strontium-90 breakthrough, so performance monitoring is essential for determining the longevity of the barrier.

Table 3-3. Volumes of High Concentration Solution Injected in 2011

Upriver Deep Injections		Volume Injected		Injection Rate (L/min)	Upriver Shallow Injections		Volume Injected		Injection Rate (L/min)
Well	Skid	Liters	Gallons		Well	Skid	Liters	Gallons	
199-N-211	Skid 2	94,614	24,997	33	199-N-212	Skid 2	312,834	82,651	98
199-N-213	Skid 1	190,267	50,269	73	199-N-214	Skid 1	213,633	56,442	67
199-N-215	Skid 2	49,693	13,129	17	199-N-216	Skid 2	43,153	11,401	14
199-N-217	Skid 1	69,019	18,235	26	199-N-218	Skid 1	140,495	37,119	44
199-N-219	Skid 2	245,207	64,784	86	199-N-220	Skid 2	112,744	29,787	38
199-N-221	Skid 1	178,322	47,113	68	199-N-222	Skid 1	187,380	49,506	59
199-N-223	Skid 2	445,078	117,590	156	199-N-224	Skid 2	93,054	24,585	31
199-N-225	Skid 1	327,443	86,511	125	199-N-226	Skid 1	320,412	84,653	101
199-N-227	Skid 2	368,538	97,368	129	199-N-228	Skid 2	347,898	91,915	109
199-N-229	Skid 1	567,078	149,822	216	199-N-230	Skid 1	90,427	23,891	30
199-N-231	Skid 2	122,721	32,423	43	199-N-232	Skid 2	338,069	89,318	106
199-N-233	Skid 1	145,336	38,398	55	199-N-234	Skid 1	200,264	52,910	63
Total		2,803,317	740,639	1,029	Total		2,400,363	634,178	761
Downriver Deep Injections		Volume Injected		Injection Rate (L/min)	Downriver Shallow Injections		Volume Injected		Injection Rate (L/min)
Well	Skid	Liters	Gallons		Well	Skid	Liters	Gallons	
199-N-236	Skid 2	334,545	88,387	123	199-N-235	Skid 2	217,573	57,483	87
199-N-238	Skid 1	389,499	102,906	143	199-N-237	Skid 1	102,013	26,952	40
199-N-240	Skid 2	85,583	22,611	34	199-N-239	Skid 2	4,508	1,191	2
199-N-242	Skid 1	51,764	13,676	20	199-N-241	Skid 1	111,249	29,392	47

Table 3-3. Volumes of High Concentration Solution Injected in 2011

Upriver Deep Injections		Volume Injected		Injection Rate (L/min)	Upriver Shallow Injections		Volume Injected		Injection Rate (L/min)
Well	Skid	Liters	Gallons		Well	Skid	Liters	Gallons	
199-N-244	Skid 2	58,565	15,473	23	199-N-243	Skid 2	86,756	22,921	37
199-N-246	Skid 1	264,818	69,965	104	199-N-245	Skid 1	246,067	65,011	104
199-N-248	Skid 2	236,036	62,361	93	199-N-247	Skid 2	22,589	5,968	10
199-N-250	Skid 1	256,661	67,810	101	199-N-249	Skid 1	230,370	60,864	97
199-N-252	Skid 2	219,167	57,904	86	199-N-251	Skid 2	435,994	115,190	184
199-N-254	Skid 1	188,940	49,918	74	199-N-253	Skid 1	153,629	40,589	65
199-N-256	Skid 2	192,445	50,844	75	199-N-255	Skid 2	95	25	0
199-N-258	Skid 1	111,086	29,349	44	199-N-257	Skid 1	509,192	134,529	215
Total		2,389,109	631,204	918	Total		2,129,271	560,115	887

Table 3-4. Differences in Volumes Injected, Based on Hourly Flow Rate Readings and Well Totalizer Data

Injection Wells	Skid	Difference in Volume (Percent)
Upriver Deep	1	2.3
	2	28.2
Upriver Shallow	1	17.2
	2	0*
Downriver Deep	1	12.5
	2	27.1
Downriver Shallow	1	-3.0
	2	38.7

Note: The difference was calculated as: [(total volume based on hourly flow rate readings – total volume based on sum of well totalizers)/ total volume based on hourly flow rate readings] × 100.

* The hourly flow rate total was used to estimate the volume received by a well without a well totalizer volume. Therefore, the difference is zero.

Table 3-5. Concentrations of Calcium, Citrate, and Phosphate in Injection Mixtures Sampled at the Skids

Injection Phase	Sample	Calcium (µg/L) ^a	Citrate (µg/L) ^b	Phosphate (µg/L) ^a
Upriver Deep Skid 1	Skid	163,000	1,762	3,843,333
	River Water	17,900	assumed to be 0	307 UD
Upriver Deep Skid 2	Skid	156,667	1,677	3,800,000
	River Water	17,400	assumed to be 0	307 UD
Upriver Shallow Skid 1	Skid	151,667	1,620	3,853,333
	River Water	17,100	assumed to be 0	307 UD
Upriver Shallow Skid 2	Skid	156,333	1,674	3,883,333
	River Water	17,200	assumed to be 0	307 UD
Downriver Deep Skid 1	Skid	156,667	1,681	3,843,333
	River Water	16,900	assumed to be 0	307 UD
Downriver Deep Skid 2	Skid	155,333	1,664	3,863,333
	River Water	17,000	assumed to be 0	307 UD
Downriver Shallow Skid 1	Skid	157,333	1,686	3,660,000
	River Water	17,100	assumed to be 0	3,070 UD
Downriver Shallow Skid 2	Skid	157,000	1,685	3,730,000
	River Water	16,900	assumed to be 0	3,070 UD

a. Average is based on three samples of injection mixture from each skid.

b. Calculated using the calcium concentration in the skid samples (corrected for the river contribution) and based on the mixture formulation, in which the citrate concentration is 2.5 times the calcium concentration.

U = undetected

D = analyte was identified in an analysis at a secondary dilution factor (i.e., dilution factor different than 1.0).

Table 3-6. Masses of Chemicals Injected in 2011

Well	Mass Injected ^a (kg)			Apatite Concentration (mg Apatite/g Sediment ^d)	Calculated Period of Performance (Years) ^e
	Calcium ^b	Citrate	Phosphate ^{b,c}		
Upriver Deep Injections					
199-N-211	13	159	360	0.799	255
199-N-213	28	335	731	1.625	519
199-N-215	7	83	189	0.420	134
199-N-217	10	122	265	0.589	189
199-N-219	35	411	932	2.070	661
199-N-221	27	314	685	1.523	486
199-N-223	63	746	1691	3.758	1200
199-N-225	49	577	1258	2.796	893
199-N-227	52	618	1400	3.111	993
199-N-229	85	999	2179	4.842	1546
199-N-231	17	206	466	1.036	331
199-N-233	22	256	559	1.241	397
Upriver Shallow Injections					
199-N-212	44	524	1215	2.699	862
199-N-214	29	346	823	1.829	584
199-N-216	6	72	168	0.372	119
199-N-218	19	228	541	1.203	384
199-N-220	16	189	438	0.973	311
199-N-222	26	304	722	1.604	512
199-N-224	13	156	361	0.803	257
199-N-226	44	519	1235	2.743	876
199-N-228	49	583	1351	3.002	958
199-N-230	12	146	348	0.774	248
199-N-232	48	566	1313	2.917	931
199-N-234	28	324	772	1.715	548
Downriver Deep Injections					
199-N-236	47	557	1292	2.872	917
199-N-238	56	654	1497	3.326	1062
199-N-240	12	142	331	0.735	235
199-N-242	7	87	199	0.442	142
199-N-244	8	97	226	0.503	161

Table 3-6. Masses of Chemicals Injected in 2011

Well	Mass Injected ^a (kg)			Apatite Concentration (mg Apatite/g Sediment) ^d	Calculated Period of Performance (Years) ^e
	Calcium ^b	Citrate	Phosphate ^{b,c}		
199-N-246	38	445	1018	2.261	722
199-N-248	33	393	912	2.026	647
199-N-250	37	431	986	2.192	700
199-N-252	31	365	847	1.881	601
199-N-254	27	318	726	1.613	515
199-N-256	27	320	743	1.652	528
199-N-258	16	187	427	0.949	303
Downriver Shallow Injections					
199-N-235	31	365	812	1.803	576
199-N-237	15	172	373	0.830	265
199-N-239	1	8	17	0.037	12
199-N-241	16	188	407	0.905	289
199-N-243	12	146	324	0.719	230
199-N-245	35	415	901	2.001	639
199-N-247	3	38	84	0.187	60
199-N-249	33	388	843	1.873	598
199-N-251	62	735	1626	3.613	1154
199-N-253	22	259	562	1.249	399
199-N-255	0	0	0	0.001	1
199-N-257	73	859	1864	4.141	1322

a. Mass injected based on well totalizer data (Table 3-3) and skid sample average concentration data (Table 3-5).

b. Calcium concentrations in samples corrected for contribution by river water. Phosphate concentrations in samples not corrected for contribution by river water.

c. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg. Wells receiving less than the target phosphate mass are identified with red text.

d. Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment. Wells with less than the target apatite concentration are identified with red text.

e. Wells with a calculated period of performance less than the 300 year expected performance period are identified with red text.

3.1.4 Pressures at Injection Wells

During injection operations, the injection well pressures were recorded hourly (Appendix C).

The injection well pressure gauges were located near the well head (Figure 2-13). Figure 3-6 (a through d) shows plots of the average injection pressure and total injected volume for each well. The higher pressures reflect a lower flow rate of the injected volume into the surrounding formation. The inverse correlation between pressure and flow rate is stronger for the deeper wells than for the shallower wells.

This is consistent with the lower permeability and lower hydraulic conductivity of the saturated Ringold Formation, in which imposed higher flow volumes build up higher pressures than in the unsaturated shallow interval. Treatment during lower river stage in the shallow wells created a condition in which there was very little to no saturation in the shallow zones. This would allow for faster flow of the solution away from the well screen during injection with less pressure buildup.

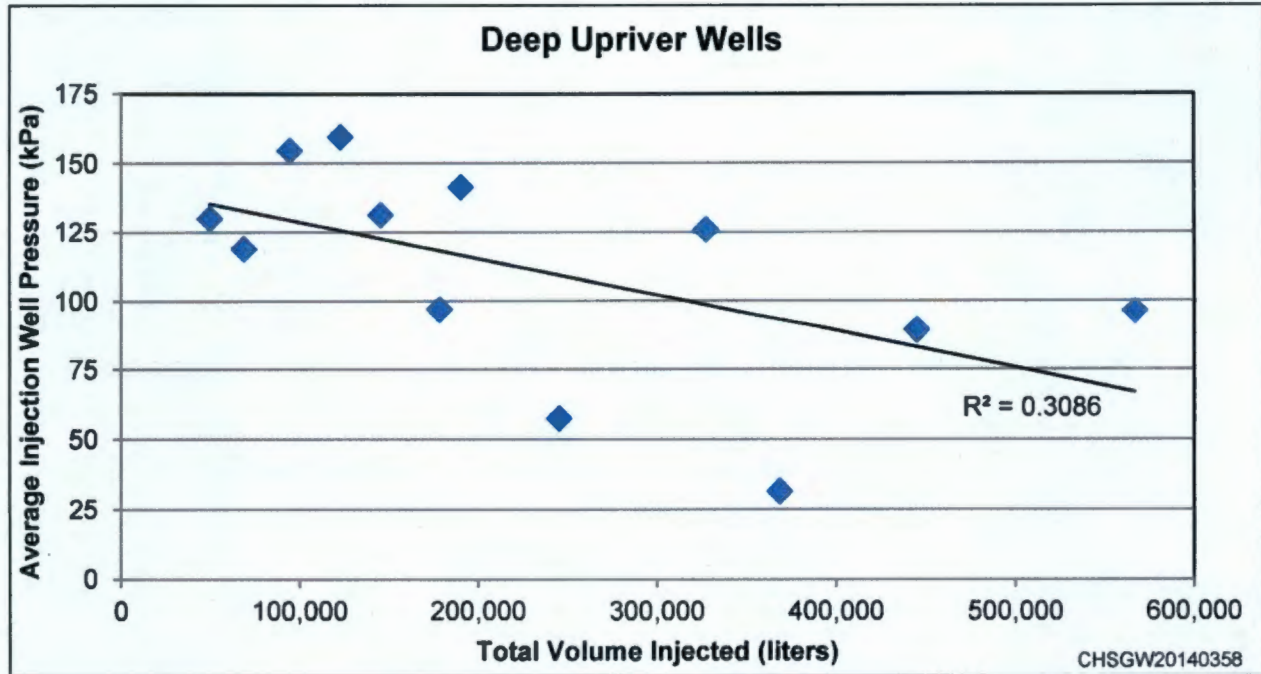


Figure 3-6a. Linear Trend of Pressure-Volume Data for Deep Upriver Injection Wells

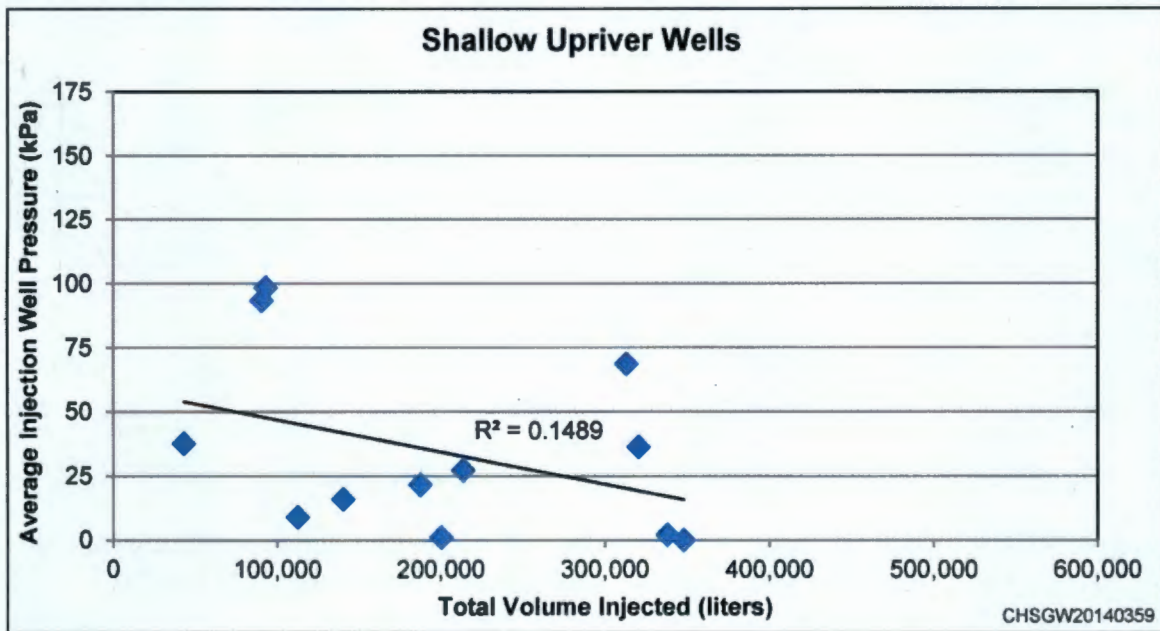


Figure 3-6b. Linear Trend of Pressure-Volume Data for Shallow Upriver Injection Wells

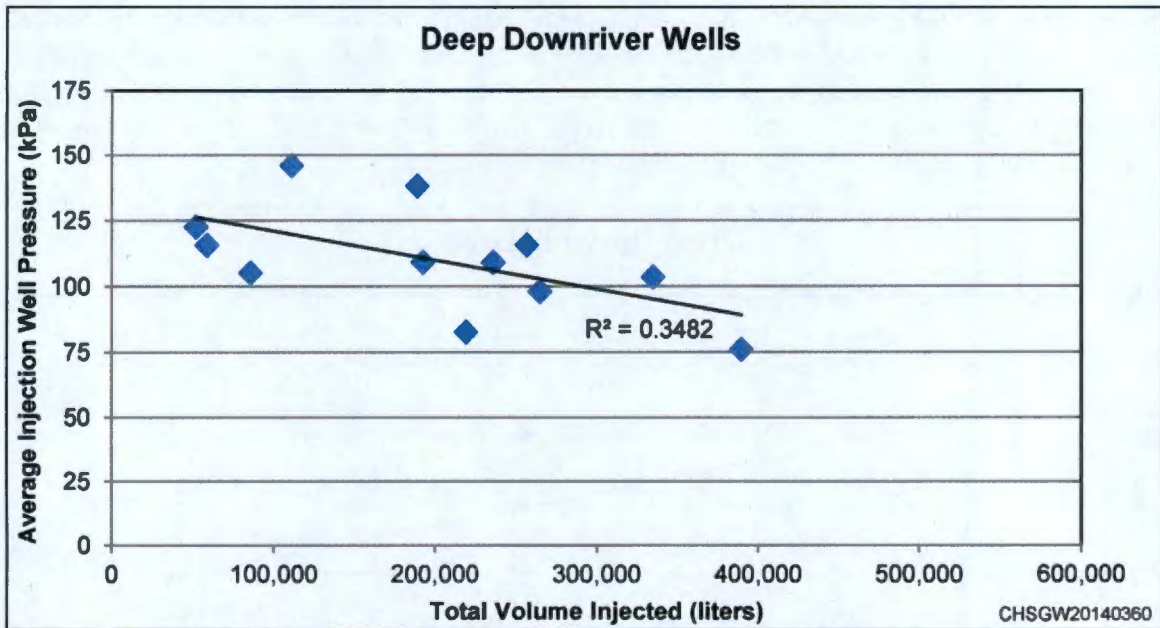


Figure 3-6c. Linear Trend of Pressure-Volume Data for Deep Downriver Injection Wells

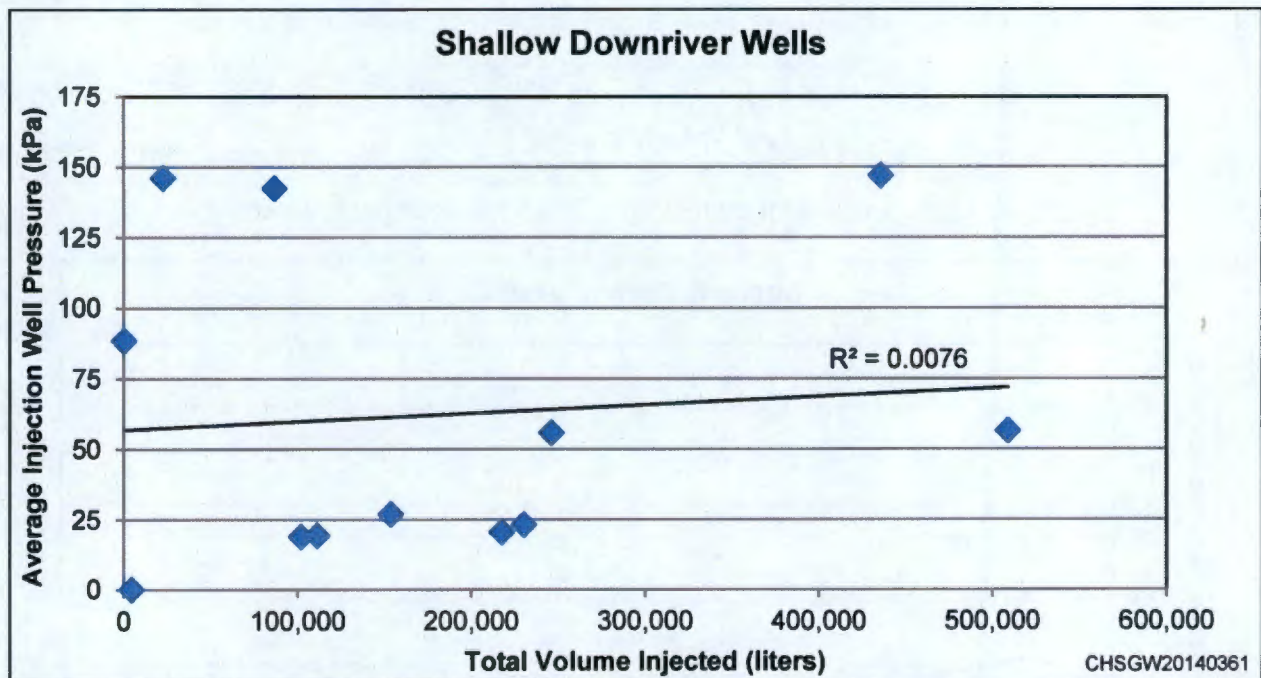


Figure 3-6d. Linear Trend of Pressure-Volume Data for Shallow Downriver Injection Wells

The pressure buildup in an injection well could push the well injection apparatus (injection piping and landing plates) up out of the well casing. If the well head injection manifold began to rise, then the operator turned off injection flow to that well and opened the packer vent valve to relieve the air pressure in the packer until the manifold lowered back into the well. The packer would then be reconnected to the air compressor and inflated, and the flow to that well would resume at a reduced rate. Figure 3-7 shows an injection well piping assembly that has risen from the well because the well was over-pressurized.

The construction of these wells with PVC casing (with smooth, almost seamless, milled joints) rather than stainless steel (with uneven, welded couplings) may have allowed the packers to slip more easily.

The pressure build up also could cause a short circuit upwelling of the injection fluid, along with formation fines (very-fine silt), along the outside of the casing to the surface. Several upwelling locations were observed adjacent to the well casings at the surface. Some of this upwelling material created an accumulation of liquid on the ground surface. For example, Figure 3-8 shows indications that injection fluid reached the surface near deep upriver Well 199-N-213 during injections. When upwelling was observed, the operator reduced injection rates to the affected wells. Upriver Wells 199-N-200 through 199-N-225 were installed in the previously excavated (now backfilled) 100-N-65 Diesel Oil Interceptor Trench waste site (petroleum burn pit) (Figure 1-7a). Most of the shallow and deep upriver wells are screened within the backfill material (estimated to have been 9 m [30 ft] deep from the current ground surface). The addition of backfill, of uncertain compaction, likely contributed to the heterogeneity and probably increased the permeable nature of the sediment fill that surrounds these wells.



Note: This photograph was taken on September 7, 2011.

Figure 3-7. Injection Well Piping that has Risen Out of a Deep Upriver Injection Well as a Result of Overpressurization during Injection of Solution



Note: This photograph was taken on September 12, 2011.

Figure 3-8. Indication that Injection Fluid Reached the Ground Surface at Deep Upriver Well 199-N-213 during Injection from September 7 to 9, 2011

Overpressurization was more common during the initial upriver injections. Balancing the flow pressure and the injection flow rate improved during subsequent phases of injection. This is consistent with the well pressure trends, which are generally more uniform for the downriver wells (Appendix C, Figures C-1 through C-4).

3.1.5 Monitoring during Injections

As required by the field test instruction (Section 6 of SGW-47614), skid solution flow rates and well pressures were measured hourly during injections, and field parameters of the injection mixture were measured every four hours (Appendix C). The skid data were recorded on the skid monitoring forms included in the apatite injection technical procedure and in the field test instruction (Section 3.1.3).

Three samples of the injection mixture were collected from each skid; one at the beginning, one at the middle, and one at the end of injections. A sample of river water also was collected from each skid at the beginning of injections. These samples were submitted to the laboratory for analysis of anions by ion chromatography and major cations by inductively coupled plasma. Field parameters (pH, specific conductance, oxidation-reduction potential, temperature, and turbidity) also were measured for each sample (Appendix D).

The field test instruction required that field parameters (specific conductance, temperature, pH, oxidation-reduction potential, and dissolved oxygen) be monitored continuously in situ at two upriver performance monitoring wells during the upriver injections and at two downriver performance monitoring wells during the downriver injections. Probes were installed in performance monitoring Wells 199-N-347 and 199-N-349, located downgradient of the upriver injection network, before and during the upriver injections. Data in these performance monitoring wells were recorded every 60 minutes (Table 3-7). Probes were installed in two downriver performance monitoring wells, one of which was Well 199-N-352, located downgradient of the downriver injection network, during and following the downriver injections. The probe in the second downriver performance monitoring well failed or was damaged during deployment. Any data recorded by this probe could not be retrieved. Data in the single downriver performance monitoring well were recorded every 15 minutes. Figures 1-7a, 1-7b, and 1-7d show screen locations and area hydrogeology for these wells.

Table 3-7. Summary of In Situ Monitoring Data

Performance Monitoring Well	Monitoring Start Date	Monitoring End Date	Monitoring Frequency (Minutes)	Depth to Water	Pressure	Temperature	Specific Conductance	pH	Barometric Pressure
199-N-347	August 24	September 19	60	N	Y	Y	Y	Y	Y
199-N-349	August 25	September 19	60	Y	Y	Y	Y	N	N
199-N-352	September 19	October 20	15	Y	Y	Y	Y	N	N

Y = yes

N = no

The two upgradient apatite injection wells nearest to each of these three performance monitoring wells are listed in Table 3-8, with the total volume injected.

Table 3-8. Upgradient Apatite Injection Wells Nearest to the In Situ Monitoring Wells

Performance Monitoring Well	Upgradient Injection Wells	Relative Depth	Injection Volume (Liter)	Injection Volume (Gallons)
199-N-347	199-N-216	Shallow	43,153	11,401
	199-N-217	Deep	69,019	18,235
199-N-349	199-N-228	Shallow	347,898	91,915
	199-N-229	Deep	567,078	149,822
199-N-352	199-N-250	Deep	256,661	67,810
	199-N-251	Shallow	435,994	115,190

The pressures and water levels recorded in the upriver performance monitoring wells are shown in Figure 3-9, and the specific conductivity recorded in the upriver performance monitoring wells is shown in Figure 3-10. Depth to water was recorded only in upriver Well 199-N-349. The pressures and water

levels recorded in the downriver performance monitoring wells are shown in Figure 3-11, and the specific conductivity recorded in the downriver performance monitoring well is shown in Figure 3-12. Depth to water was recorded only in downriver Well 199-N-352.

Monitoring data were not collected in any of the injection wells during the injections.

3.1.5.1 Injection Monitoring: Water Levels

Upriver Shallow Injection Wells. During the injections into the upriver shallow wells, the ambient water level remained below the screened intervals of the shallow injection wells during the injections and the following 7-day apatite reaction period (Section 3.1.2). As a result, the apatite fluid was injected into the portion of the aquifer that was unsaturated at that time. Although the water table elevation in the downgradient performance monitoring Well 199-N-349 temporarily increased as a result of the injections, it declined to ambient levels approximately 80 hours after the injections started (Table 3-9). During this period of mounding, the water level remained at least 0.3 m (1 ft) above the average elevation of the bottom of the shallow screens (i.e., at least 0.3 m [1 ft] above 118.8 m) for 20 hours. Assuming that the water level mounding in the injection wells was of at least equal height and duration, a water elevation of at least 0.3 m (1 ft) above the screen bottom indicates that at least the lower 20 percent of the 1.5 m (5 ft) long screened interval was saturated. The average half-life for citrate biodegradation is 50 hours (PNNL-16891), so approximately one quarter of the citrate would have released calcium to form apatite in the shallow aquifer zone during this time. The groundwater conductivity in the performance monitoring wells (which are screened in the deep aquifer zone) remained high throughout the reaction period, suggesting that the injected chemicals remained locally within the groundwater long enough to form apatite at and below the ambient water table. However, the specific conductance can be elevated by the presence of reaction products and may not be indicating the presence of apatite-forming chemicals.

Downriver Shallow Injection Wells. During the injections into the downriver shallow wells, the ambient water level remained within the screened intervals of the shallow injection wells during the injections and the 7-day apatite reaction period. It appears that the water level mounding created in the downgradient performance monitoring Well 199-N-352 during the injections lasted approximately 56 hours. During this time, the water level was above the average elevation of the top of the shallow screen (i.e., above 119.1 m) for 42 hours. Assuming that the water level mounding in the injection wells was of at least equal height and duration, 42 hours is long enough for almost half of the calcium to become available to react with the phosphate, based on the citrate half-life. It is possible that approximately half of the potential apatite mass (based on the injection volume) was emplaced in the full thickness of the shallow aquifer zone. The groundwater conductivity in the performance monitoring well remained high throughout the reaction period, suggesting that the injected chemicals remained locally within the groundwater long enough to form apatite within part of the shallow aquifer zone and at and below the ambient water table. However, the specific conductance can be elevated by the presence of reaction products and may not be indicating the presence of apatite-forming chemicals.

Upriver and Downriver Deep Injection Wells. During the injections into the upriver and downriver deep wells, the ambient water level remained above the screened intervals of the deep injection wells during the injections and the 7-day apatite reaction periods, so the apatite fluid was injected directly into the saturated portion of the aquifer. Artificially elevated water levels above the ambient water level were recorded in downgradient performance monitoring Wells 199-N-349 and 199-N-352 as a result of the injections. The mounding lasted approximately 66 hours upriver and 44 hours downriver and declined rapidly following cessation of injections. The groundwater conductivity in the downgradient performance monitoring wells remained elevated throughout the injection and apatite reaction periods, suggesting that apatite forming chemicals remained locally within the upriver and downriver deep aquifer zone.

However, the specific conductance can be elevated by the presence of reaction products and may not be indicating the presence of apatite-forming chemicals.

During the groundwater mounding resulting from the deep upriver injections, the water level in the downgradient performance monitoring Well 199-N-349 was at least 0.3 m (1 ft) above the average bottom of the shallow screens (i.e., at least 0.3 m [1 ft] above 118.8 m) for 50 hours and above the average top of the shallow screens (i.e., above 120.3 m) for 34 hours. During the groundwater mounding resulting from the deep downriver injections, the water level in the downgradient performance monitoring Well 199-N-352 was at least 0.3 m (1 ft) above the average bottom of the shallow screens (i.e., at least 0.3 m [1 ft] above 117.6 m) for 44 hours and above the average top of the shallow screens (i.e., above 119.1 m) for 41 hours. Assuming that the water level mounding in the injection wells was of at least equal height and duration, it is possible that apatite also was formed in the shallow aquifer zone during these injections. However, many of the deep injection wells received low injection volumes, so excess chemical reagents may not have been available to treat the shallow zone during the mounding.

The magnitude of the temporary mounding in response to the deep downriver injections at downriver performance monitoring Well 199-N-352 was similar to that in response to the deep upriver injections in upriver performance monitoring Well 199-N-349. The deep injection wells upgradient of these two monitoring wells both received more than 227,100 L (60,000 gal) of apatite-forming fluid (Table 3-8).

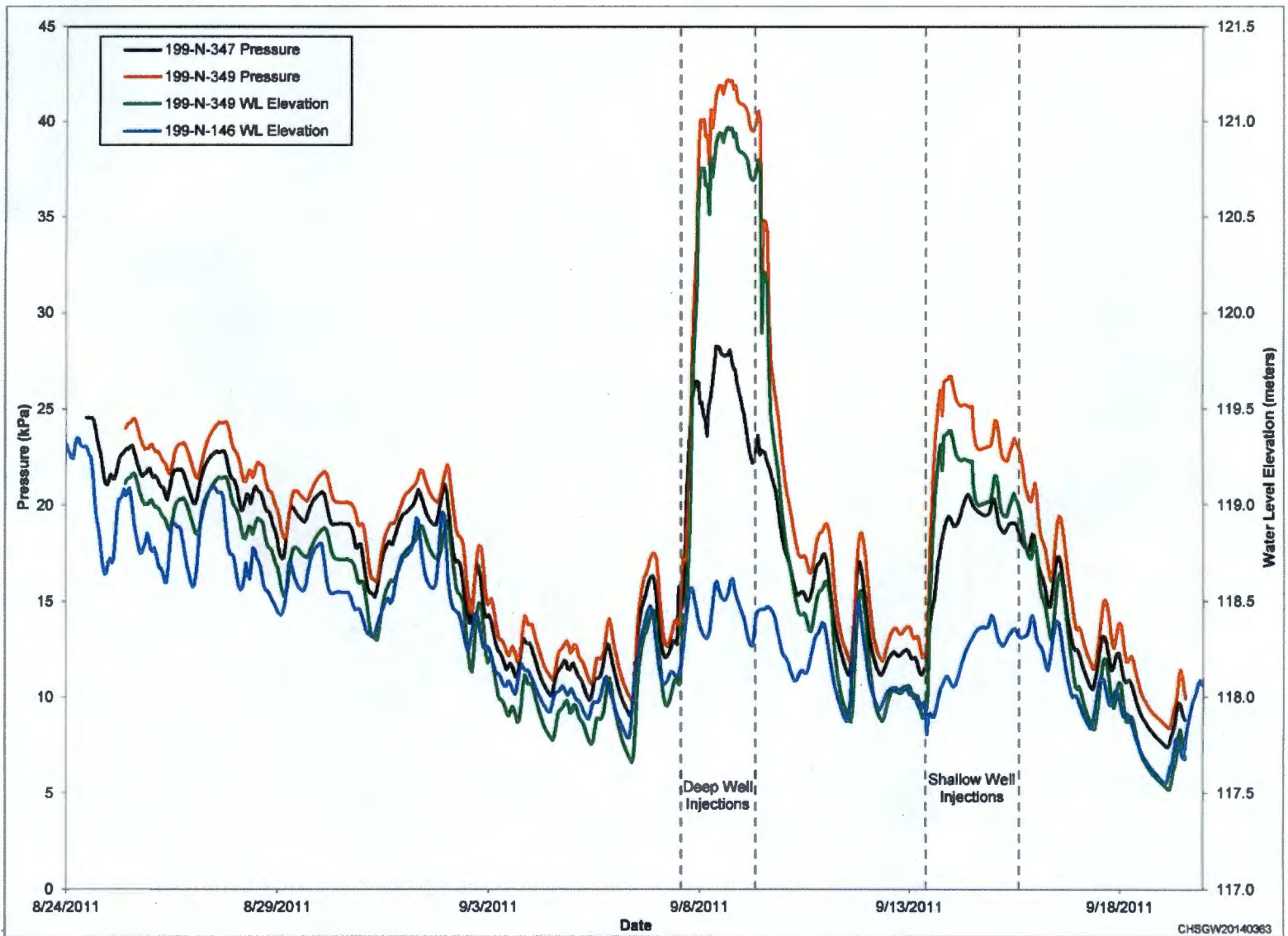


Figure 3-9. Pressures and Water Levels in Upriver Performance Monitoring Wells 199-N-347 and 199-N-349 during Upriver Injections

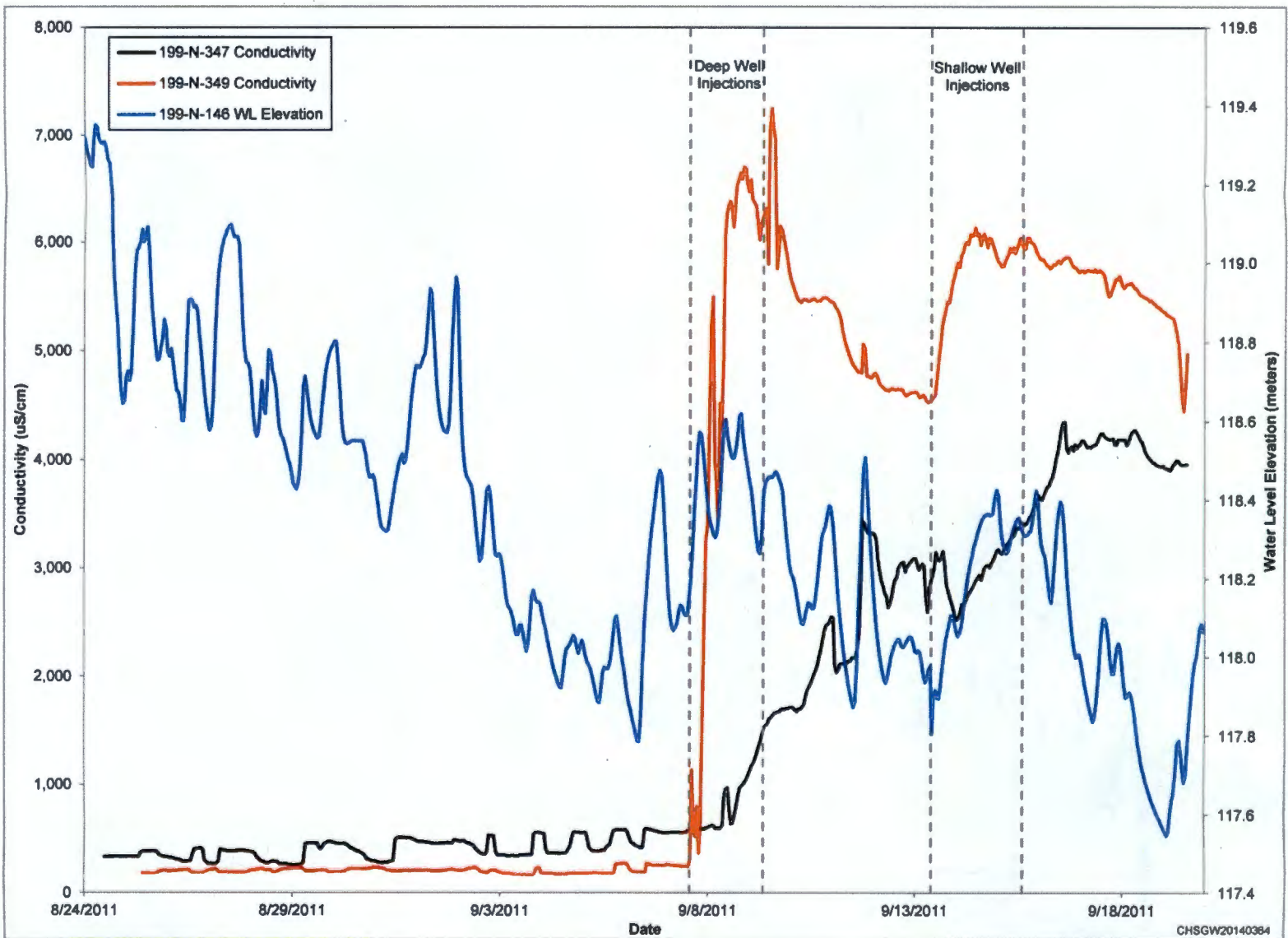


Figure 3-10. Specific Conductivity in Upriver Performance Monitoring Wells 199-N-347 and 199-N-349 during Upriver Injections

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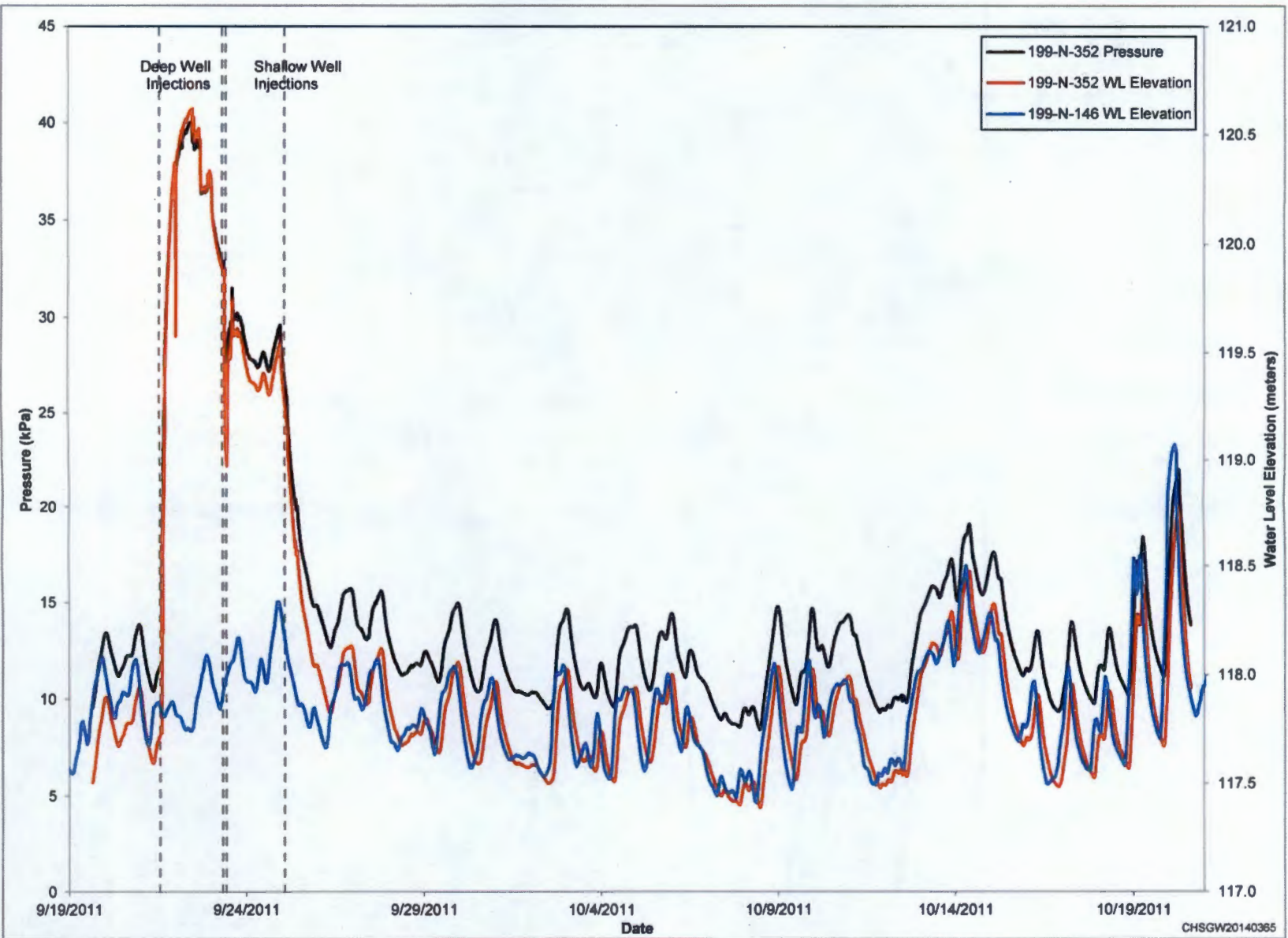


Figure 3-11. Pressures and Water Levels in Downriver Performance Monitoring Well 199-N-352 during Downriver Injections

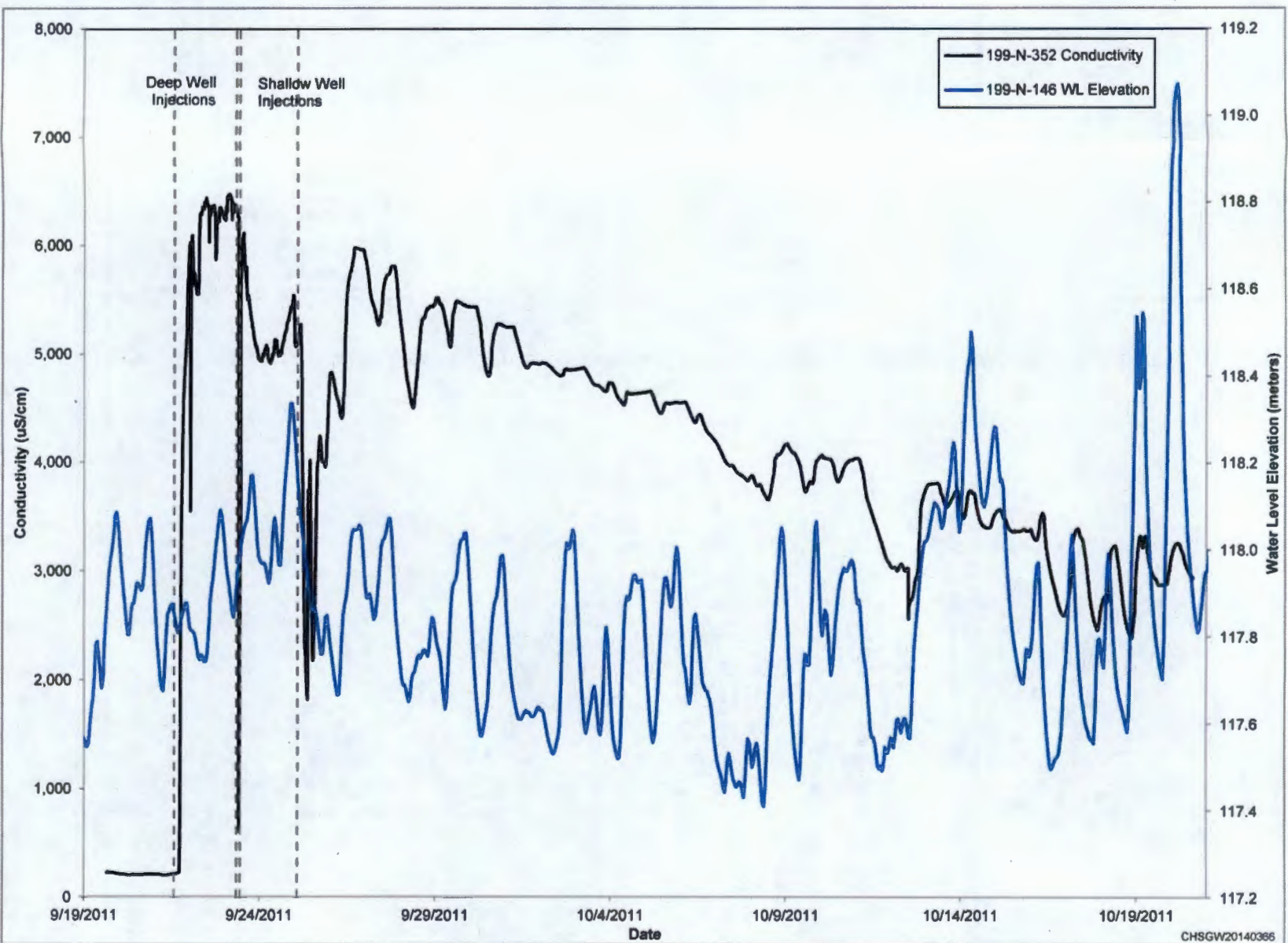


Figure 3-12. Specific Conductivity in Downriver Performance Monitoring Well 199-N-352 during Downriver Injections

3.1.5.2 Injection Monitoring: Specific Conductivity

The specific conductivity in the upriver and downriver performance monitoring wells increased during the apatite injections (Figure 3-10 and Figure 3-12, respectively). Specific conductivity increased relatively quickly at upriver performance monitoring Well 199-N-349 and downriver performance monitoring Well 199-N-352 following the start of injection into the deep wells. The more gradual increase in upriver performance monitoring Well 199-N-347 suggests that Well 199-N-347 is in a relatively low flow zone. It also may reflect more mixing of groundwater with the relatively low volume of apatite fluid injected into deep upgradient Well 199-N-217 (Table 3-8). The delay in the apparent arrival of the apatite-forming solution at performance monitoring Well 199-N-347, based on the delayed increase in the groundwater specific conductivity, also may be because Well 199-N-347 is screened near, but outside of, the backfilled petroleum burn pit (100-N-65) region (Figure 1-7a). All of the injection wells in the barrier network upgradient of Well 199-N-347 are screened within the backfill material, which likely is more permeable than the native aquifer material. As a result, solutions injected into these wells would likely flow into regions within the backfilled excavation before migrating outward, away from the disturbed area, thus delaying the arrival time in outlying wells. This is not the case for upriver performance monitoring Well 199-N-349 and downriver performance monitoring Well 199-N-352, which both show very little delay in conductivity increases.

The increases in specific conductivity in the two upriver performance monitoring wells during the shallow well injections were similar to those for the deep well injections (Figure 3-10). The elevated specific conductivity in the downriver performance monitoring well declined slowly following injections (Figure 3-12). The relatively high conductivity during at least a couple of weeks suggests that the injected chemicals remained local long enough to form apatite at and below the ambient water table. However, the specific conductance can be elevated by the presence of reaction products and may not be indicating the presence of apatite-forming chemicals.

3.1.5.3 Injection Monitoring: Radiological Contamination

As described in Section 1.2.2, the radiological contamination detected during drilling of the barrier injection network wells generally defines a vertical region that extends a few meters above and below the average ambient water table (approximately 119 m amsl in 2011) (Figure 1-7). The upriver shallow wells are screened just above the 2011 average water table, and the downriver shallow wells are screened just below the 2011 average water table. The upriver deep wells are screened just above the 2011 low water table, and the downriver deep wells are screened across the 2011 low water table.

Upriver Barrier. In the upriver treated portion of the barrier, the vertical extent of detected radiological contamination measured during borehole drilling ranges from approximately 115 m to 120.8 m amsl and averages approximately 118 m (Figure 1-7a and Figure 1-7b). The average ambient water table elevation was approximately 118 m in September 2011. Water level and conductivity increases in downgradient performance monitoring Well 199-N-349 (as described above) suggest that apatite forming chemicals were present in the aquifer interval from approximately 119.1 m amsl to the bottom of the deep injection well screen interval at approximately 115.8 m amsl and that the apatite barrier formed across this vertical interval will be capable of capturing the strontium-90 in groundwater moving through this zone. However, as noted above, the elevated conductivity in Well 199-N-349 may be caused by residual reaction products rather than apatite-forming chemicals. In addition, many wells did not receive the minimum target injection volume, which may make the barrier less efficient in some areas.

Downriver Barrier. In the downriver treated portion of the barrier, the vertical extent of detected radiological contamination measured during borehole drilling ranges from approximately 114.4 m to 120.2 m amsl and averages approximately 118 m (Figure 1-7c and Figure 1-7d). Water level and conductivity increases in downgradient performance monitoring Well 199-N-352 (as described above) suggest that apatite forming chemicals were present in the aquifer interval from approximately

119.9 m amsl to the bottom of the deep injection well screen intervals at approximately 114.7 m amsl and that the apatite barrier formed across this vertical interval will be capable of capturing the strontium-90 in groundwater moving through this zone. However, as noted above, the elevated conductivity in Well 199-N-352 may be caused by residual reaction products rather than apatite-forming chemicals. In addition, many wells did not receive the minimum target injection volume, which may make the barrier less efficient in some areas.

3.1.6 Monitoring Post-Injection

Three sets of aqueous samples were collected from groundwater performance monitoring wells and aquifer tubes following injection of the apatite-forming fluid. The three sets of upriver samples were collected 19 hours, two weeks, and four weeks after completion of all upriver injections. The three sets of downriver samples were collected 57 hours, four weeks, and five weeks after completion of all downriver injections. The samples were analyzed for anions, major cations and metals, and gross beta. Samples from the upriver locations also were analyzed for TPH-diesel. Selected results are provided in Table 3-10. All of the results are reported in Appendix G. Trend plots of specific conductivity and phosphate are shown in Figure 3-13; trend plots of calcium and phosphate are shown in Figure 3-14; and trend plots of gross beta and specific conductivity are shown in Figure 3-15.

3.1.6.1 Monitoring Post-Injection: Performance Wells

The post-injection results are compared to the baseline (pre-injection) results in this section. For the seven performance monitoring wells installed as part of the barrier well network extension in 2010, only one pre-injection sample (or one sample plus a duplicate sample) was collected.

Specific Conductivity and Phosphate. At the performance monitoring wells, the specific conductivity and phosphate concentrations were both elevated in the first post-injection sample, compared to the concentrations in the baseline (pre-injection) sample from the same well. The specific conductivity and phosphate concentrations followed similar declining trends in subsequent samples (Figure 3-13). These data reflect the relatively simultaneous arrival of the injection fluids and the phosphate, or the arrival of residual reaction products.

Calcium. The calcium concentrations in the post-injection samples were lower than the concentrations in the baseline (pre-injection) samples (or comparable, in Wells 199-N-96A and 199-N-347) (Figure 3-14). At seven of the wells, the calcium concentrations continued to decline during the post-injection monitoring period. At Well 199-N-350, the post-injection calcium concentration was highest in the four-week sample (but still less than in the baseline sample). The high concentration formulation is calcium-poor and relies on calcium naturally present in the aquifer sediments as a source for apatite formation (i.e., 75 percent of the calcium used in apatite formation is desorbed from aquifer sediments) (Sections 2.3 and 2.5.1 of PNNL-19572). The injected citrate complexes with the calcium that is present in the groundwater and that desorbs from sediments and prevents it from being available for apatite formation until the citrate degrades. The decrease in calcium in post-injection samples in 2011 suggests that the naturally available calcium was initially complexed with the injected citrate and then used to form apatite.

During application of the calcium-poor high concentration formulation in the original segment of the barrier in 2008, calcium concentrations were temporarily elevated in performance monitoring wells following injections (Figure 3-16). The difference between the calcium trends in 2008 and 2011 may indicate that the Hanford formation (present in the original segment but not the upriver and downriver segments) contained more natural calcium than the Ringold Formation; or that the calcium-rich low concentration formulation injected in 2007 affected 2008 calcium concentrations in wells in the original segment.

Table 3-9. Elevations of Screened Intervals and Water Levels During Injections in 2011

Injection Phase	Average Elevation of Screen Top	Average Elevation of Screen Bottom	Average Elevation of Ambient Water Level in Well 199-N-146 during Injections	Average Elevation of Ambient Water Level in Well 199-N-146 during Injections Plus 7 Days	Maximum Elevation of Mounding in Downgradient Performance Monitoring Well	Approximate Duration of Mounding above Average Ambient Water Level in Downgradient Performance Monitoring Well during Injections	Approximate Duration of Mounding above Average Shallow Well Screen Bottom in Downgradient Performance Monitoring Well
	m amsl	m amsl	m amsl	m amsl	m amsl	Hours	Hours
Upriver Deep	117.9	115.8	118.4	118.2	121.0	66	54
Upriver Shallow	120.3	118.8	118.2	118.0	119.4	80	52
Downriver Deep	116.8	114.7	117.9	117.9	120.5	44 ^a	45
Downriver Shallow	119.1	117.6	118.1	117.9	119.7	56	67 ^b

a. Injections in the shallow wells began before the mounding from the injections in the deep wells had declined to ambient levels.

b. Duration until elevated water level declines to ambient water level following injections; ambient water level remains above bottom of shallow screen.

amsl = above mean sea level

Well 199-N-123, a performance monitoring well at the upriver end of the original barrier segment, appears to have been impacted by upriver injections in 2011. At this well, calcium concentrations were elevated in 2011 following the upriver injections. The 2011 increase in concentration was comparable to the 2007 and 2008 increases (Figure 3-16).

Gross Beta. Gross beta activity was higher than the baseline (pre-injection) activity in the first post-injection sample in five wells (199-N-96A, 199-N-347, 199-N-349, 199-N-351, and 199-N-353) and lower than the baseline in the other three wells (Figure 3-15). In all of the upriver and downriver wells, any elevated gross beta activity following injections declined within two weeks. This relatively rapid decline is similar to that seen in performance monitoring wells for the original barrier segment (Figure 3-16). (Note that Well 199-N-123 at the upriver end of the original segment and Well 199-N-147 at the downriver end of the original segment appear to have temporary increases in gross beta activity caused by the 2011 injections.) Temporary increases in the gross beta activity reflect temporary increases in the strontium-90 concentrations as a result of injection of the apatite-forming solutions. Strontium-90 concentrations were not analyzed in the three post-injection samples. Gross beta activity was used as the surrogate for strontium-90.

Metals/Cations and Anions. After the 2011 injections, concentrations of metals/cations and anions temporarily increased. Most of these concentrations returned to near or below pre-injection levels within a few weeks to months (based on sampling in the four weeks following the injections and the performance monitoring in May 2012). Strontium concentrations declined in all of the upriver and downriver performance monitoring wells following the 2011 injections (Figure 3-17). Arsenic remains elevated above pre-injection concentrations in four wells (199-N-348, 199-N-350, 199-N-351, and 199-N-353). Arsenic was detected in aquifer tubes 116mArray-2A, C7881, and 116mArray-8A during injections and once in C7881 and 116mArray-8A following injections. Although phosphate and sodium concentrations have declined, they remained slightly elevated above pre-injection concentrations in most of the wells and aquifer tubes.

Dissolved Oxygen. Citrate biodegradation results in temporary reducing conditions in the treatment zone. The reducing conditions result in decreased dissolved oxygen concentrations and increases in redox-sensitive trace metal concentrations (e.g., iron, manganese, and aluminum) (Section 2.7.2 of PNNL-17429). During the four weeks of post-injection monitoring in 2011 at the performance monitoring wells, the dissolved oxygen concentrations were less than the most recent pre-injection concentration in all wells except Well 199-N-348. In the upriver wells, the most recent pre-injection concentration ranged from 1,560 to 6,260 $\mu\text{g/L}$ (most were measured in April 2010). During performance monitoring in 2012 and 2013, dissolved oxygen concentrations fluctuated, exceeding the pre-injection concentration at least once in each well. (Well 199-N-96A shows fluctuating dissolved oxygen concentrations since 2001.) In the downriver wells, the most recent pre-injection concentration ranged from 9,260 to 10,150 $\mu\text{g/L}$ (measured in July 2010). In these wells, dissolved oxygen concentrations slowly increased during 2012 and 2013 but did not approach the pre-injection concentrations.

Turbidity. The baseline (pre-injection) samples from the performance monitoring wells had turbidity values ranging from 2.79 to 23.4 nephelometric turbidity units (NTUs) (all but Well 199-N-96A had values greater than 5 NTUs). Turbidity was measured in the 4 week post-injection samples from the upriver wells and the 2 week and 4 week post-injection samples from the downriver wells. With the exception of two wells (199-N-351 and 199-N-352), these post-injection samples had turbidity values less than 5 NTUs. Turbidity values in the two-week and four-week samples from Well 199-N-352 were 48.9 NTUs and 10.2 NTUs, respectively; the turbidity value in the four-week sample from Well 199-N-351 was 6.13 NTUs. The general decrease in turbidity following the injections was attributed to the use of

high quality (food grade) chemicals and ultra high-purity water ($<0.5 \mu\text{S}/\text{cm}$) to make the chemical injection mixtures.

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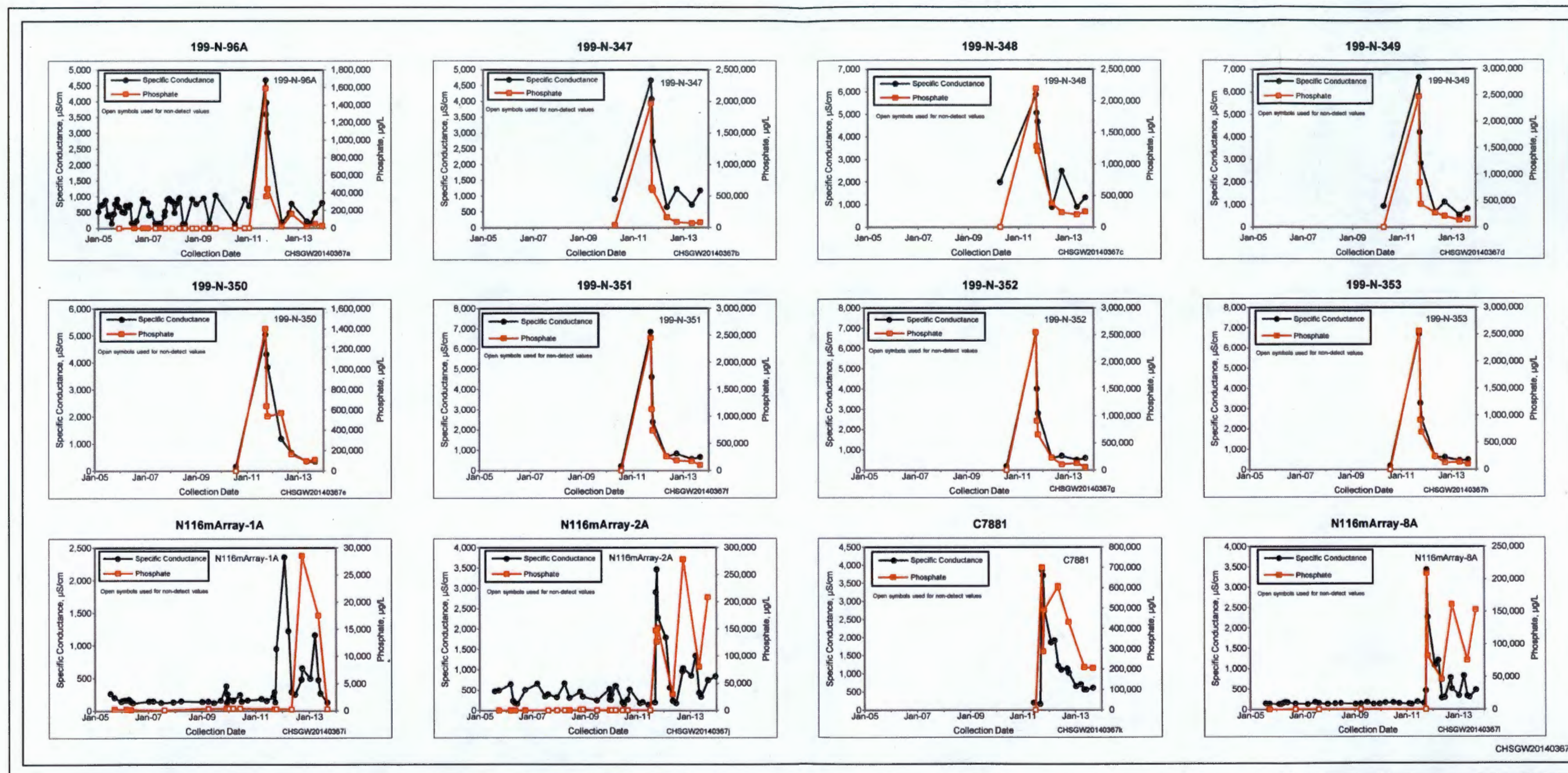


Figure 3-13. Specific Conductance and Phosphate Trends in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

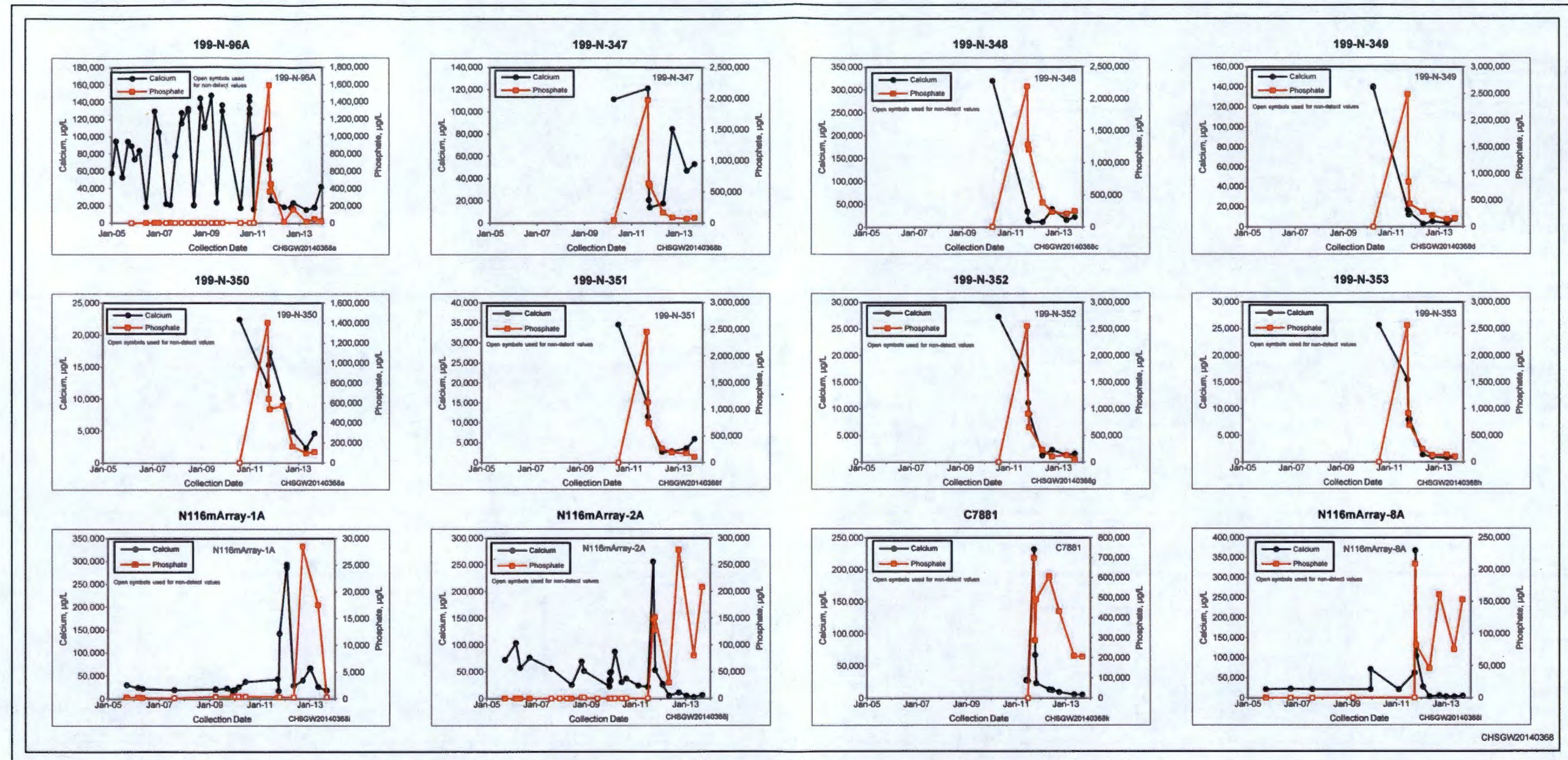


Figure 3-14. Calcium and Phosphate Trends in Upriver and Downriver Performance Wells and Aquifer Tubes

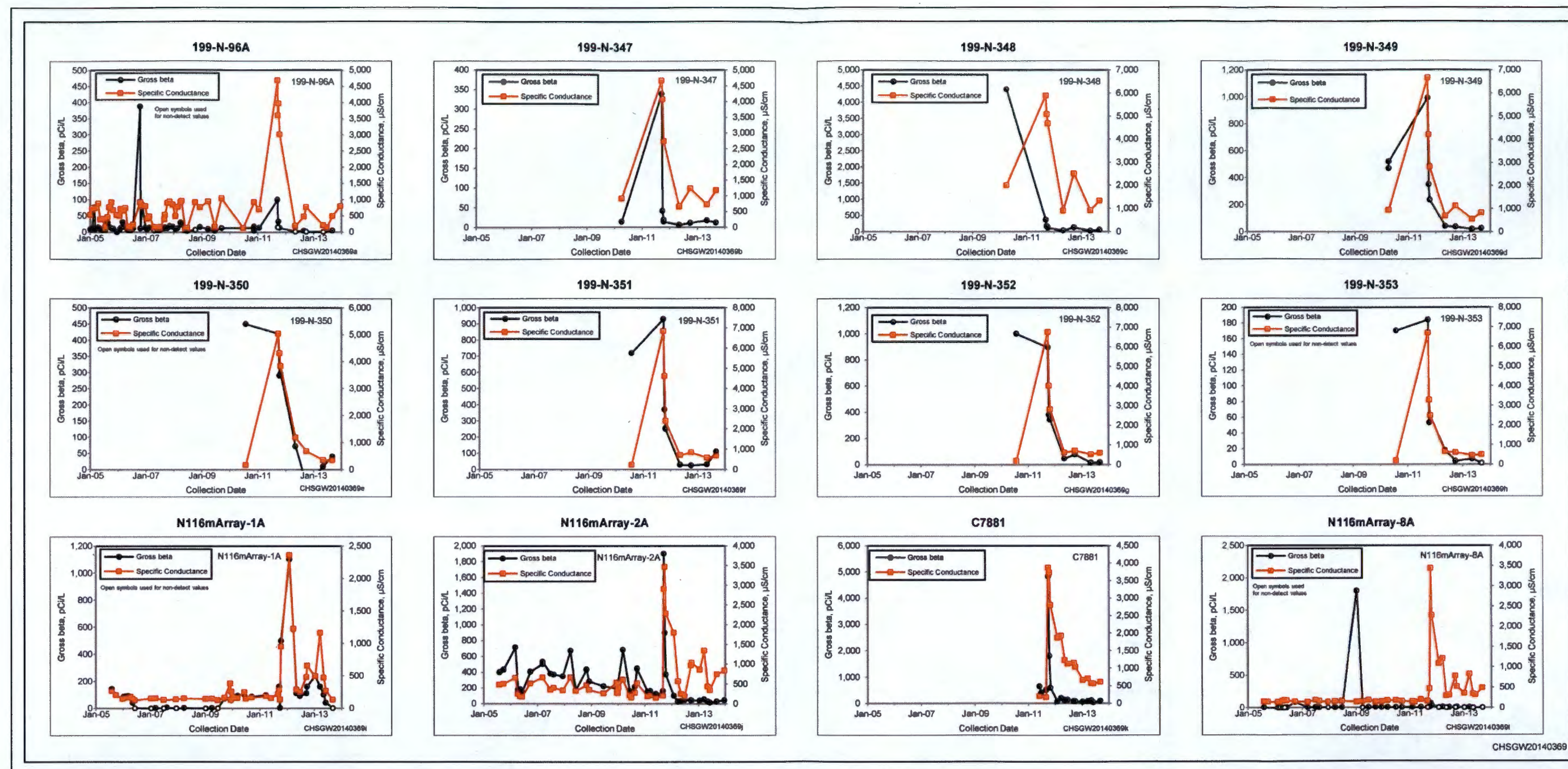


Figure 3-15. Gross Beta and Specific Conductance Trends in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

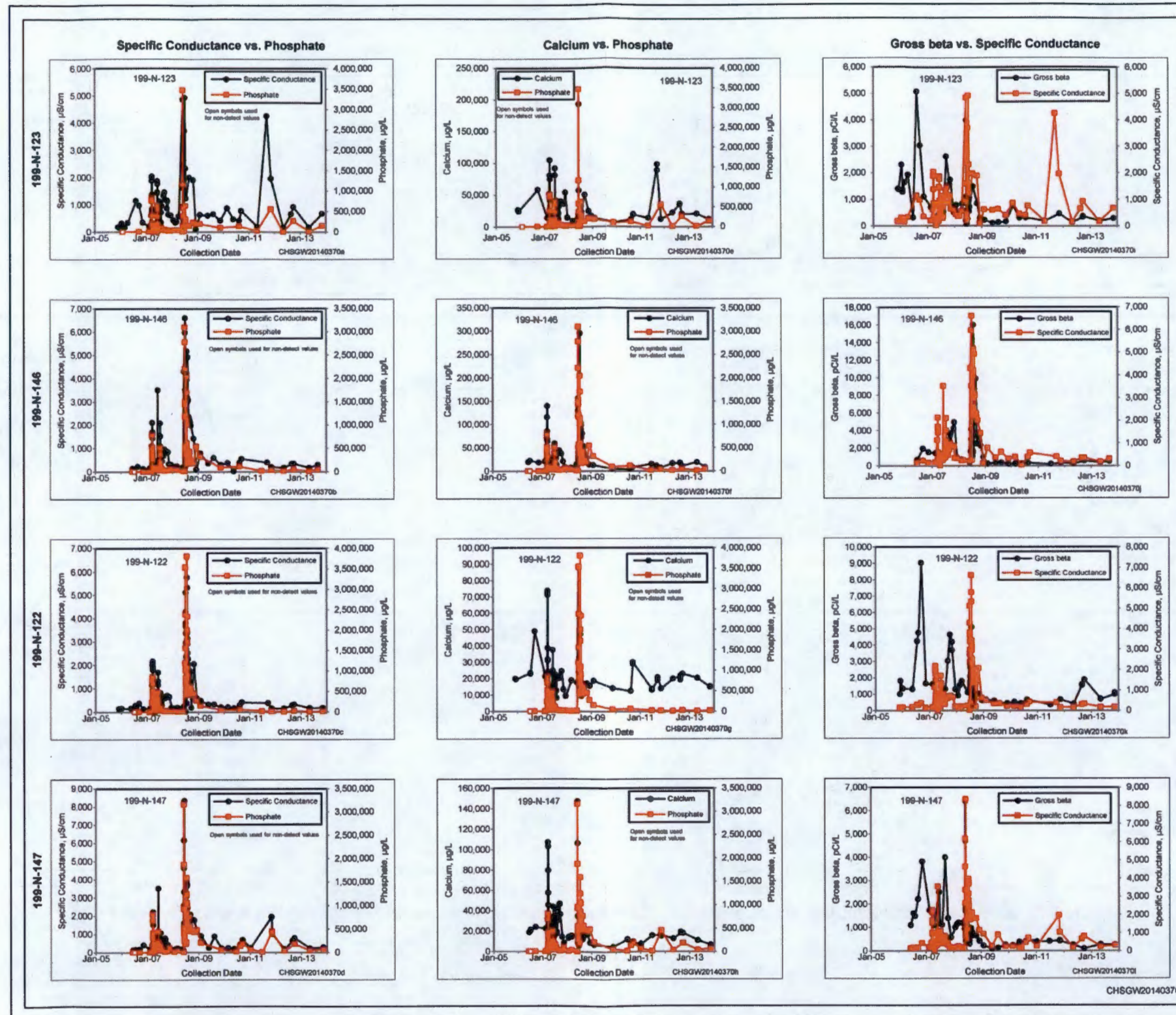
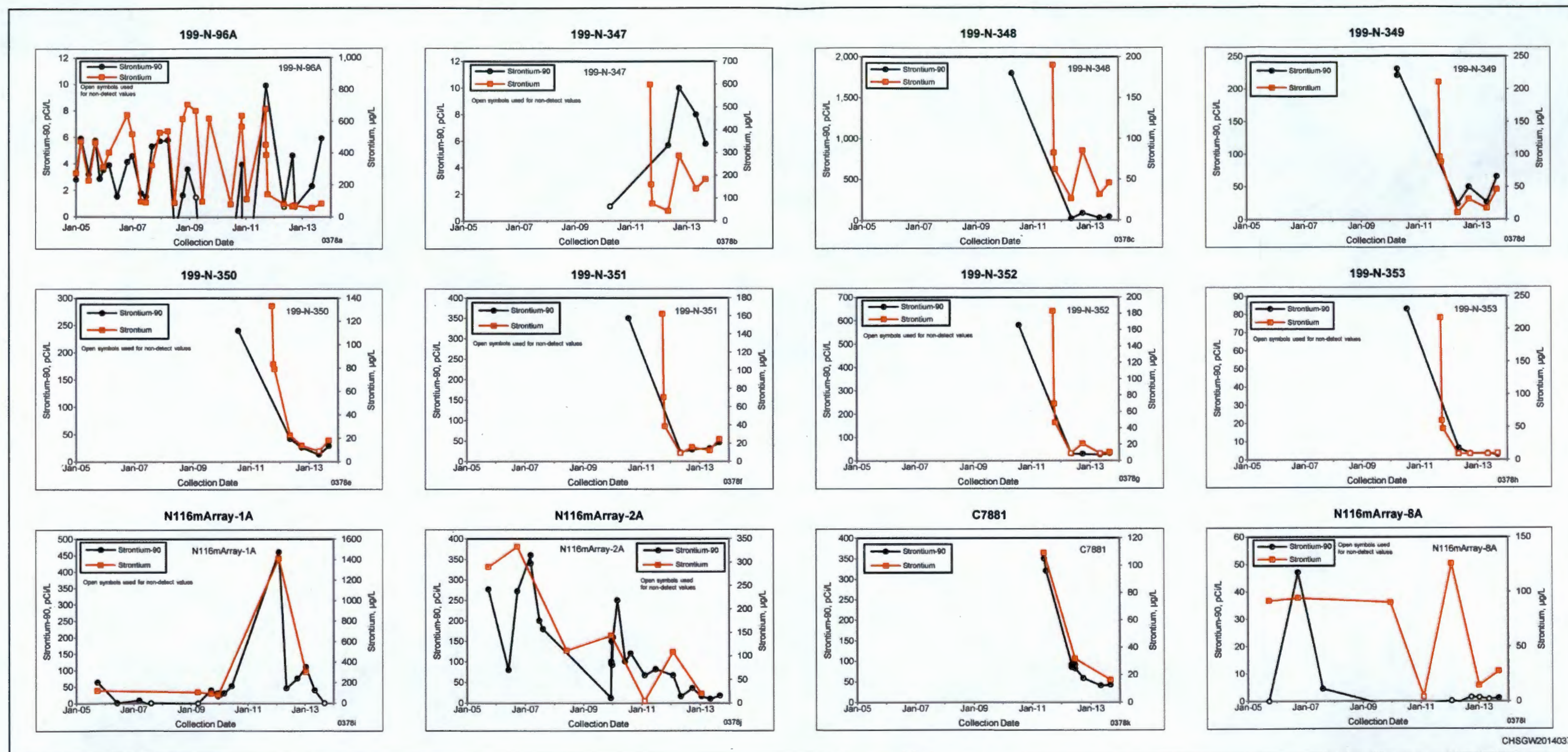


Figure 3-16. Specific Conductance and Phosphate Trends, Calcium and Phosphate Trends, and Gross Beta and Specific Conductance Trends in Original Segment Performance Monitoring Wells



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Figure 3-17. Strontium and Strontium-90 Trends in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

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Conductivity. Injection of the higher purity mixture may have resulted in slightly lower increases in conductivity compared to increases following previous injections. The maximum conductivity measured in monitoring wells during 2011 post-injection monitoring ranged from 4,669 $\mu\text{S}/\text{cm}$ to 6,841 $\mu\text{S}/\text{cm}$; the maximum value in 2008 was 8,335 $\mu\text{S}/\text{cm}$. The characteristic odor from the degradation of citrate was present in most initial samples and more so in the two-week samples (162895, October 13, 2011, "100/300 Area Unit Managers Meeting Minutes" Attachment 1, "Groundwater and Source Operable Units; Facility Deactivation, Decontamination, Decommission, and Demolition (D4); Interim Safe Storage (ISS); Field Remediation (FR); and Mission Completion").

3.1.6.2 Monitoring Post-Injection: Aquifer Tubes

At upriver aquifer tube N116mArray-1A, specific conductivity was elevated in the four-week sample and highest in the sample from February 1, 2012. Although phosphate was not detected during this time, elevated phosphate concentrations were detected in September 2012 and May 2013. Calcium also was elevated in the four-week sample and highest in the sample from February 2012. At upriver aquifer tube N116mArray-2A, specific conductivity was elevated in three post-injection samples, but it was highest in the two-week sample and still elevated in the sample from January 31, 2012. Although phosphate was elevated during this time, higher phosphate concentrations were detected in September 2012 and September 2013. Calcium was highest in the first post-injection sample and still elevated in the two-week sample.

At downriver aquifer tube C7881, specific conductivity was elevated in all three post-injection samples, and highest in the first sample. Although phosphate was elevated during this time (highest in the first sample), elevated phosphate concentrations were detected in four monitoring samples from 2012 and 2013. Calcium was highest in the first post-injection sample and still elevated in the two-week sample. At downriver aquifer tube N116mArray-8A, specific conductivity was elevated in all three post-injection samples, but highest in the two-week sample. Phosphate was elevated in the two-week and four-week samples (highest in the two-week sample) and in the four monitoring samples from 2012 and 2013. Calcium was elevated in the two-week and four-week samples (highest in the two-week sample).

Table 3-10. Selected Analytical Results for Monitoring Wells and Aquifer Tubes During the First Four Weeks after Apatite Injections

Well Name/ Well Identification	Date Sampled	Gross Beta (pCi/L)	Specific Conductivity ($\mu\text{S}/\text{cm}$)	Phosphate ($\mu\text{g}/\text{L}$)	TPH- Diesel ($\mu\text{g}/\text{L}$)
All Upriver Injections Completed on September 15, 2011 at 14:25					
199-N-96A/A9882	09/16/2011 10:35	100.00	4,681.00	1,590,000.00	70.00 U
	09/28/2011 09:00	32.90	3,966.00	362,000.00	80.00 U
	10/13/2011 08:40	13.60	3,013.00	448,000.00	85.00 U
199-N-347/C7441	09/16/2011 10:13	340.00	4,669.00	1,970,000.00	80.00 U
	09/28/2011 09:34	41.70	4,072.00	632,000.00	80.00 U
	10/13/2011 09:15	14.40	2,738.00	598,000.00	85.00 U
	10/13/2011 09:15	19.10	2,738.00	601,000.00	85.00 U
199-N-348/C7440	09/16/2011 09:40	360.00	5,878.00	2,190,000.00	80.00 U
	09/28/2011 10:01	171.00	5,068.00	1,280,000.00	80.00 U
	10/13/2011 10:20	119.00	4,668.00	1,200,000.00	85.00 U
199-N-349/C7439	09/16/2011 10:00	990.00	6,643.00	2,480,000.00	70.00 U
	09/28/2011 10:46	352.00	4,192.00	837,000.00	80.00 U
	10/13/2011 11:28	236.00	2,814.00	426,000.00	85.00 U

**Table 3-10. Selected Analytical Results for Monitoring Wells and Aquifer Tubes
During the First Four Weeks after Apatite Injections**

Well Name/ Well Identification	Date Sampled	Gross Beta (pCi/L)	Specific Conductivity (μS/cm)	Phosphate (μg/L)	TPH- Diesel (μg/L)
N116mArray-1A	09/16/2011 08:55	160.00	284.00	307.00 U	80.00 U
	09/28/2011 10:20	2.87 Y	130.60	307.00 U	80.00 U
	10/13/2011 09:50	498.00	948.00	307.00 U	85.00 U
N116mArray-2A	09/16/2011 09:21	1,900.00	2,902.00	147,000.00	80.00 U
	09/28/2011 11:05	896.00	3,461.00	126,000.00	80.00 U
	10/13/2011 10:53	367.00	2,279.00	152,000.00	85.00 U
All Downriver Injections Completed on September 25, 2011 at 2:00					
199-N-350/C7443	09/27/2011 09:05	420.00	5,036.00	1,400,000.00	NA
	10/12/2011 09:50	290.00	4,307.00	638,000.00	NA
	10/27/2011 08:56	296.00	3,827.00	537,340.00	NA
199-N-351/C7444	09/27/2011 09:30	930.00	6,841.00	2,450,000.00	NA
	10/12/2011 10:48	370.00	4,604.00	1,130,000.00	NA
	10/27/2011 09:45	255.00	2,386.00	731,633.00	NA
	10/27/2011 09:45	249.00	2,386.00	740,741.00	NA
199-N-352/C7445	09/27/2011 09:56	895.00	6,739.00	2,550,000.00	NA
	10/12/2011 15:00	380.00	4,003.00	908,000.00	NA
	10/27/2011 10:37	342.00	2,797.00	649,666.00	NA
199-N-353/C7446	09/27/2011 10:21	184.00	6,689.00	2,560,000.00	NA
	10/12/2011 12:12	53.00	3,266.00	911,000.00	NA
	10/27/2011 11:18	61.50	2,476.00	690,143.00	NA
C7881*	09/27/2011 10:42	4,830.00	3,862.00	699,000.00	NA
	10/12/2011 10:16	1,800.00	3,715.00	287,000.00	NA
	10/27/2011 09:22	586.00	2,795.00	490,791.00	NA
N116mArray-8A	09/27/2011 11:12	7.80	464.00	307.00 U	NA
	10/12/2011 11:47	67.00	3,432.00	209,000.00	NA
	10/27/2011 10:56	36.00	2,271.00	81,562.50	NA

* Aquifer tube C7881 replaced aquifer tube N116mArray-7A.

NA = not analyzed (TPH-diesel analyzed only in upriver wells and aquifer tubes)

U = analyzed for but undetected

Y = result suspect

3.2 Impacts of Apatite Treatment on Strontium-90

The upriver and downriver apatite barrier performance monitoring wells and aquifer tubes were sampled semiannually in 2012 and 2013. The samples were filtered and analyzed for strontium-90, gross alpha, and gross beta activity; TPH-diesel; anions; cations and metals; and field parameters. The results for strontium-90 in groundwater performance monitoring wells in the upriver and downriver barrier expansions are provided in Table 3-11.

Table 3-11. Strontium-90 Concentrations in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

Well Name	Number of Baseline Samples	Number of Baseline Nondetects	Strontium-90 Concentration (pCi/L)									Percent Reduction in Strontium-90 (Baseline to Fall 2013) ⁿ	
			Minimum Detected Baseline	Maximum Baseline	Fall 2011 ^b			Spring 2012	Fall 2012	Spring 2013	Fall 2013	Minimum Baseline	Maximum Baseline
Upriver Apatite Permeable Reactive Barrier													
			04/06/10		09/16/11	09/28/11	10/13/11	05/06/12, 05/09/12	09/27/12	05/06/13	09/06/13		
199-N-96A	56	8	1.54 ^a	37.9 ^a	50	16.45	6.8	0.76 U ^c	0.76 U ^d	2.3	5.9	-283	84
199-N-347	1	1	7 ^{b,e}	7 ^{b,e}	170	20.85	7.2, 9.55	5.7	10	8.5	5.8	17	17
199-N-348	1	0	1,800	1,800	180	85.5	59.5	20	88	28	41	98	98
199-N-349	2	0	220	230	495	176	118	24	50	27	66	70	71
N116mArray-1A	16	3	0.836 ^h	63.7 ^h	80	1.435 Y	249	45	75	39	0.35 U	o	o
N116mArray-2A	18	0	12 ⁱ	360 ⁱ	950	448	183.5	16	36	10	18	o	o
Downriver Apatite Permeable Reactive Barrier													
			07/28/10, 07/29/10		09/27/11	10/12/11	10/27/11	05/09/12	10/01/12	05/06/13	09/06/13		
199-N-350	1	0	240	240	210	145	148	42	26	13	29	88	88
199-N-351	1	0	350	350	465	185	127.5, 124.5	22	29	32	46	87	87
199-N-352	1	0	580	580	447.5	190	171	30	29	26	31	95	95
199-N-353	1	0	83	83	92	26.5	30.75	6.5	3.4 U	3.5	2.8	97	97
N116mArray-7A	3	0	240 ^j	330									
C7881 ^m	2	0	320	350 ^j	2,415	900	293	88	58	40	42	o	o
N116mArray-8A	5	3	4.5 ^k	47.1 ^k	3.9	33.5	18	-0.12 U	1.5 U	0.8 U	1.1	o	o

Table 3-11. Strontium-90 Concentrations in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

Well Name	Number of Baseline Samples	Number of Baseline Nondetects	Strontium-90 Concentration (pCi/L)								Percent Reduction in Strontium-90 (Baseline to Fall 2013) ^a	
			Minimum Detected Baseline	Maximum Baseline	Fall 2011 ^b		Spring 2012	Fall 2012	Spring 2013	Fall 2013	Minimum Baseline	Maximum Baseline

a. Between 1995 and 2011, the maximum baseline was measured on 12/06/1995; the minimum detected baseline was measured on 06/13/2006 and 06/22/2007.

b. Based on gross beta measurement divided by two to approximate strontium-90 concentration.

c. Gross beta = 2.3 pCi/L. The strontium-90 concentration was 1.1 U pCi/L.

d. Gross beta = 1.5 pCi/L. A routine groundwater monitoring sample from 08/27/12 had a strontium-90 concentration of 4.60 pCi/L.

e. The strontium-90 concentration was 1.1 U pCi/L. The gross beta concentration, 14 pCi/L, was divided by two to approximate the strontium-90 concentration of 7 pCi/L.

f. Average of two results for gross beta: 249 pCi/L and 255 pCi/L.

g. Average of two results for strontium-90: 85 pCi/L and 91 pCi/L.

h. Between 2005 and 2010, the maximum baseline was measured on 09/28/2005; the minimum detected baseline was measured on 06/06/2006.

i. Between 2005 and 2011, the maximum baseline was measured on 03/12/2007; the minimum baseline was measured on 12/11/2009.

j. Between 2005 and 2011, the maximum baseline was measured on 06/02/2011; the minimum baseline was measured on 08/09/2007.

k. Between 2005 and 2011, the maximum baseline was measured on 09/26/2006; the minimum detected baseline was measured on 08/13/2007.

l. Not used

m. C7881 installed in 2010 to replace 116mArray-7A.

n. The percent reduction in strontium-90 concentration is calculated as $(([\text{baseline value}] - [\text{Fall 2013 value}]) / [\text{baseline value}]) \times 100$. For Well 199-N-96A the minimum baseline value used in the calculation was the lowest detected value. For Well 199-N-96A, the calculations for spring and fall 2012 used half of the reported nondetect value (i.e., 0.76/2).

o. The percent reduction in strontium-90 concentration is based on groundwater samples from the performance monitoring wells and is not calculated for aquifer tubes.

U = analyzed for but not detected

Y = result is suspect

3.2.1 Results for Injection Wells

The injection wells used in 2011 have not been sampled since the pre-injection baseline data were collected in 2010.

3.2.2 Results for Performance Monitoring Wells

The upriver and downriver performance monitoring wells were sampled in May and September of 2012 and in May and September of 2013. The strontium-90 concentrations measured in these samples were compared to the minimum and maximum pre-injection strontium-90 concentrations at each well. Only two wells (199-N-96A and 199-N-349) had more than one pre-injection sample result; for the other six wells, the minimum and maximum pre-injection strontium-90 concentrations were the same.

In the upriver monitoring wells, the percent reduction in strontium-90 concentrations in September 2013 (the end of the second year following the injections) ranged from 17 percent (Well 199-N-347) to 98 percent (Well 199-N-348). The relatively low percent reduction in Well 199-N-347 reflects comparison of the low baseline strontium-90 concentration (the strontium-90 concentration was nondetect, and the strontium-90 concentration estimated from gross beta was 7.0 pCi/L) to the low strontium-90 concentrations measured during performance monitoring (ranging from 5.7 pCi/L to 10 pCi/L) (Table 3-11). Because the strontium-90 concentrations in the pre-injection sample and the fall 2013 sample from Well 199-N-347 are below the DWS, the percent reduction in the strontium-90 concentration is not plotted on Figure 3-18a.

Well 199-N-347 appears to be located in a low-flow zone. The low strontium-90 concentrations indicate that contaminated groundwater does not appear to flow through the aquifer in the vicinity of this well. Well 199-N-347 is at the edge of the strontium-90 groundwater plume where concentrations are generally at or less than the DWS (8 pCi/L). The volumes of apatite solution injected in the deep (Well 199-N-217) and shallow (Well 199-N-216) injection wells upgradient of Well 199-N-347 were lower than the volumes injected upgradient of the other three upriver monitoring wells. During the upriver injections, the increase in specific conductivity at Well 199-N-347 lagged behind the increase at Well 199-N-349 (Figure 3-10). These observations suggest that this localized area of the aquifer has relatively low permeability or may be influenced by the petroleum burn pit backfill in which the upgradient injection wells were completed (Section 3.1.5) and would not be a priority for additional injections of apatite-forming solutions.

In the downriver monitoring wells, the percent reduction in strontium-90 concentrations in September 2013 ranged from 87 percent (Well 199-N-351) to 97 percent (Well 199-N-353) (Figure 3-18b). The volume of apatite solution injected in the deep (Well 199-N-244) injection well upgradient of performance monitoring Well 199-N-351 was lower than the volumes injected in the deep wells upgradient of the other three downriver performance monitoring wells.

3.2.3 Results for Aquifer Tubes

The upriver and downriver aquifer tubes specified for monitoring were sampled in May and September of 2012 and in May and September of 2013 (Table 3-11). At the furthest upriver aquifer tube, N116mArray-1A (downgradient from Wells 199-N-222, 199-N-223, and 199-N-348), strontium-90 concentrations have declined from a pre-injection maximum of 63.7 pCi/L to nondetect in the fall of 2013, although the strontium-90 concentration was 460 pCi/L in February 2012 and 110 pCi/L in January 2013. At the second upriver aquifer tube, N116mArray-2A (downgradient from Wells 199-N-231 and 199-N-232), strontium-90 concentrations have declined from a pre-injection maximum of 360 pCi/L to 18 pCi/L in the fall of 2013. The gradual decline in strontium-90 concentrations at this location began prior to the 2011 injections.

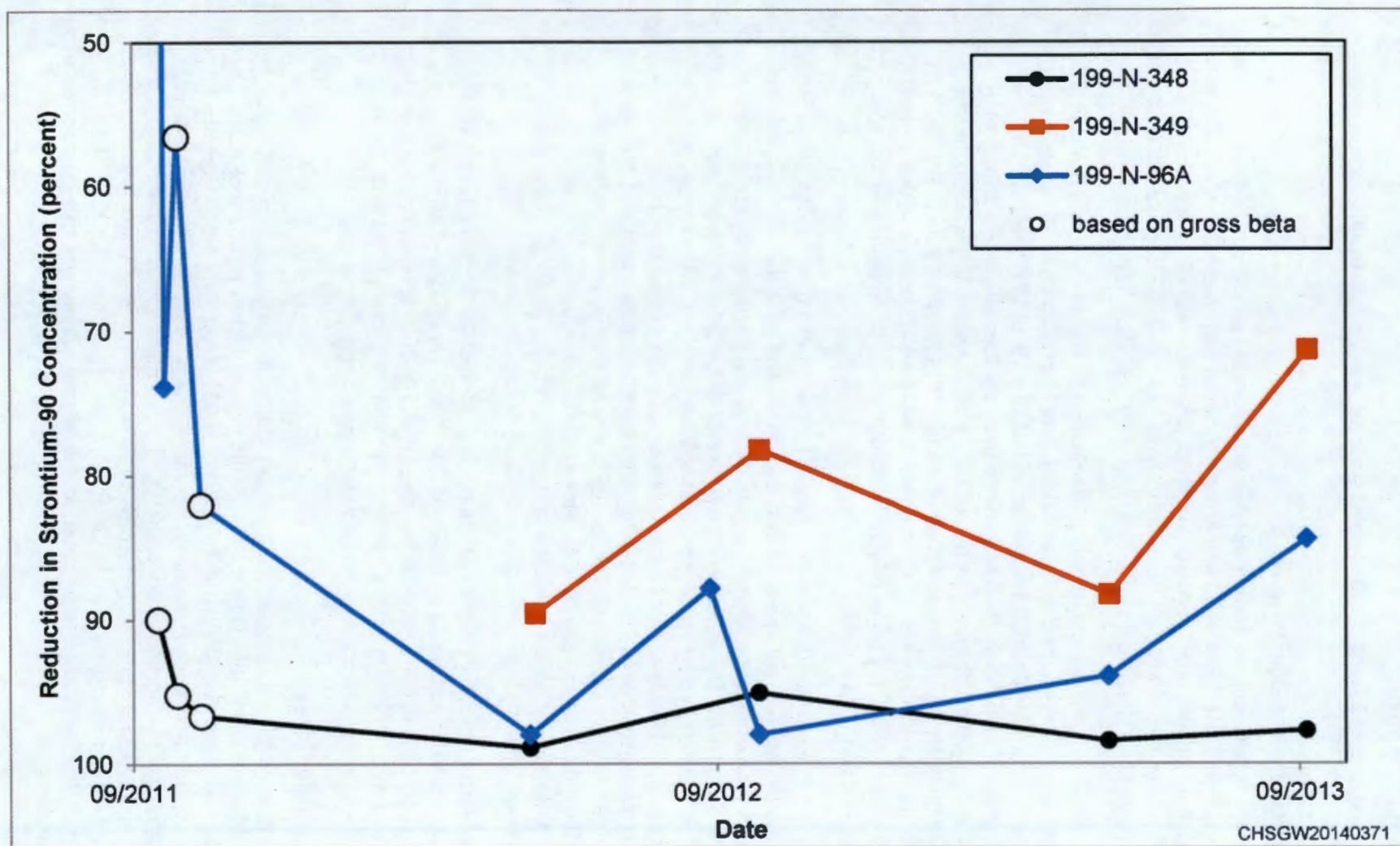


Figure 3-18a. Percent Reduction in Strontium-90 Concentrations in Upriver Performance Monitoring Wells, based on Comparison on 2012 and 2013 Measurements to Pre-Injection Measurements

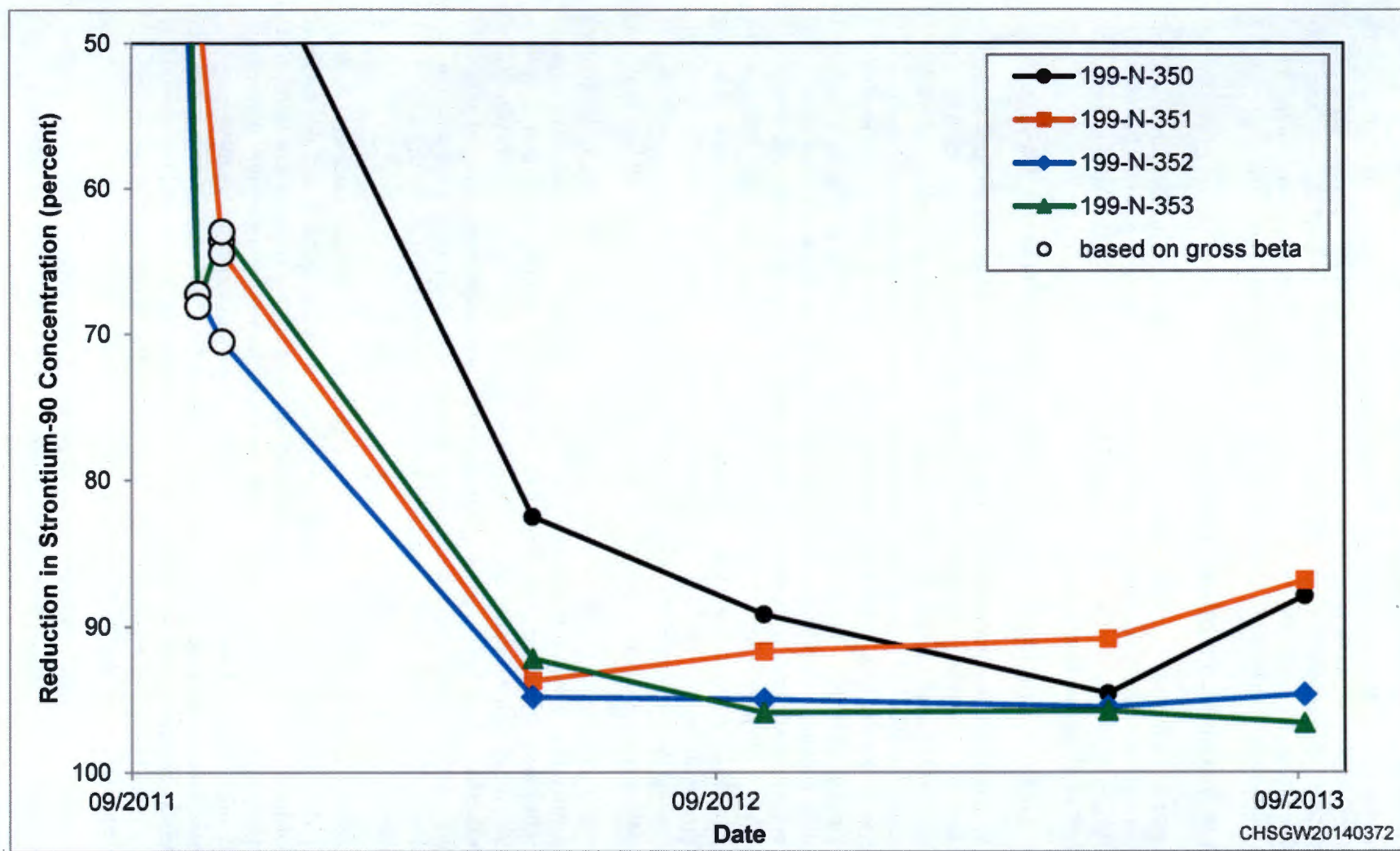


Figure 3-18b. Percent Reduction in Strontium-90 Concentrations in Downriver Performance Monitoring Wells, based on Comparison of 2012 and 2013 Measurements to Pre-Injection Measurements

At the downriver aquifer tube C7881 (downgradient from Wells 199-N-240 and 199-N-241), strontium-90 concentrations have declined from a pre-injection maximum of 350 pCi/L to 42 pCi/L in the fall of 2013. (Strontium-90 concentrations at aquifer tube N116mArray-7A, which was replaced by C7881, were less than the pre-injection maximum at C7881.) At the furthest downriver aquifer tube, N116mArray-8A (downgradient from Wells 199-N-253 and 199-N-254), strontium-90 concentrations have declined from a pre-injection maximum of 47.1 pCi/L to 1.1 pCi/L in the fall of 2013.

3.3 Evaluation of Design Optimization Objectives

As described in Section 2.1 of this report, the DOS had six objectives. In this section, the fourth objective is presented as two separate objectives. The bases for evaluating each objective, as provided in the DOS, are included in Section 2.1. The unstated objective identified in Section 2.1 also is evaluated in this section. The objectives are described as follows:

1. Refine application of the high concentration calcium-citrate-phosphate solution over a larger scale.

The 2011 injections demonstrated that six injection wells could be simultaneously injected with the high concentration calcium-citrate-phosphate solution using the injection skids developed for larger-scale injections. Although the total volumes of apatite solution injected by each skid were comparable during the upriver and downriver injections, the volumes injected into each well were variable. The primary reason for the variability is heterogeneities in the formation at the injection point. Pressure buildup within some injection wells and short-circuiting of the apatite-forming solution to the surface along the well casing likely reflect the non-uniformity of the subsurface permeability. Data are not available to evaluate whether controlling the flow to individual wells during the injections would have reduced the variability in the volumes (e.g., by stopping the flow to wells that had received 227,000 L [60,000 gal] of solution). Many of the wells in the upriver injection network are completed in the backfilled petroleum burn pit excavation (Figure 1-7a and Figure 1-7b) which will also change the flow characteristics at those wells. Data are not available to evaluate whether the injections successfully emplaced solution laterally to the target radius of influence.

The injection wells were designed to target the shallow Hanford formation and the deeper Ringold Formation in the variably saturated zone (Section 1.9.1.3 of DOE/RL-2009-32). The shallow screens were systematically placed at the approximate depth (3.0 to 4.6 m [10 to 15 ft] bgs) expected for the water table during typical higher water levels, and the deeper screens were systematically placed at the approximate depth (5.2 to 7.3 m [17 to 24 ft] bgs) expected for average water levels (Figure 1-9 and Figure 1-10 in DOE/RL-2009-32). Post-installation geologic data interpretation indicates that most of the shallow and deep wells used for the 2011 injections were screened in the Ringold Formation (Figure 1-7).

In the upriver segment of the barrier, the shallow screens were above the average water table in 2011, and the deep screens were above the low water table in 2011. In the downriver segment, the shallow screens are just below the average water table in 2011 and the deep screens are at the low water table in 2011. The highest strontium-90 concentrations tend to be near the average water table, decreasing below and above this elevation (Figure 1-7). When the water table is elevated, strontium-90 is mobilized from the deep vadose zone. This strontium-90 is likely to re-sorb to sediment closer to the average water table when the water levels decline. The groundwater contaminated with strontium-90 would have been saturating the average water table interval more frequently than the highest or lowest water level intervals, and thus more strontium-90 was sorbed at this elevation.

The injection well network configuration (alternating shallow and deep screens) adequately bounded the zone of water table fluctuation and the most likely interval of strontium-90 contamination flux in

groundwater moving through the region. The injection wells therefore were suitable for treating the strontium-90 groundwater plume migrating toward the Columbia River. Two years after the 2011 injections, monitoring at the performance monitoring wells, which are screened in the deeper zone, indicates that strontium-90 concentrations have been reduced by at least 70 percent in all seven of the wells with pre-injection concentrations that exceeded the DWS. Strontium-90 concentrations have declined in all four aquifer tubes monitored along the upriver and downriver segments.

After the 2011 injections, concentrations of metals/cations and anions temporarily increased. Most of these concentrations returned to near or below pre-injection levels within a few weeks to months (based on sampling in the four weeks following the injections and the performance monitoring in May 2012). Arsenic remains elevated above pre-injection concentrations in four wells. Although phosphate and sodium concentrations have declined, they remained slightly elevated above pre-injection concentrations in most of the wells and aquifer tubes.

2. Test the effectiveness of high concentration calcium-citrate-phosphate injection in previously untested sediment to compare with areas that received sequential injections of low then high concentration calcium-citrate-phosphate injections.
 - Impacts Over Time. The injection wells in the original segment of the apatite barrier were injected with the low concentration formulation of the apatite solution from February through June 2007 and with the high concentration formulation in July 2008 (Table 1-3). One year after the final injections, the strontium-90 concentrations measured at the performance monitoring wells (Wells 199-N-122, 199-N-123, 199-N-146, and 199-N-147) trended downward. However, after two years, small increases in strontium-90 were observed (PNNL-20252, *100-NR-2 Apatite Treatability Test: An Update on Barrier Performance*). The remedial objective was a greater than 90 percent reduction in the strontium-90 concentrations in the performance monitoring wells (DOE/RL-2005-96). In August 2010, only one well (199-N-122) showed a reduction in strontium-90 concentration greater than 90 percent; the other three showed reductions ranging from 83 to 89 percent of the maximum baseline concentration (Table 3.1 in PNNL-20252).

The injection wells in the upriver and downriver segments were injected with the high concentration formulation of the apatite solution in September 2011. One year after the final injections, the reduction in strontium-90 concentrations in the upriver wells ranged from 78 to 95 percent in three wells; the fourth well (199-N-347) had a pre-treatment baseline concentration below the DWS and is at the edge of the groundwater plume) (Table 4-7 in DOE/RL-2013-13, *Calendar Year 2012 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump-and-Treat Operations, and 100-NR-2 Groundwater Remediation*). Two years after the final injections, the reduction in strontium-90 concentrations ranged from 71 to 98 percent in the three upriver performance monitoring wells that initially exceeded the DWS (Table 3-11). One year after the final injections, the reduction in strontium-90 concentrations in the four downriver performance monitoring wells ranged from 89 to 100 percent (Table 4-8 in DOE/RL-2013-13). Two years after the final injections, the reduction in strontium-90 concentrations ranged from 87 to 97 percent (Table 3-11).

Variability in the strontium-90 concentrations in the performance monitoring wells following injections may reflect local variability in flow rates, flow direction (into and away from the river) influenced by nearby annual and diurnal river level elevations, volume of apatite solution injected upgradient, and lithology (Section 2.4.2 of DOE/RL-2010-29). The monitoring wells also may be influenced by groundwater from untreated or partially treated areas between the barrier and the river (Section 3.1 of PNNL-20252).

- Influence of River Stage. Strontium-90 concentrations at performance monitoring wells appear to vary with river stage elevation. Concentrations typically are higher in the fall, when the river stage is lower, and lower in the spring, when the river stage is higher. This implies that during low river stage, when the groundwater containing dissolved strontium-90 contamination is flowing toward the river, the groundwater at the monitoring wells is less diluted, and that during high river stage, when river water is flowing inland at higher elevations, the groundwater at the monitoring wells may be mixed with river water, diluting the strontium-90 concentrations.

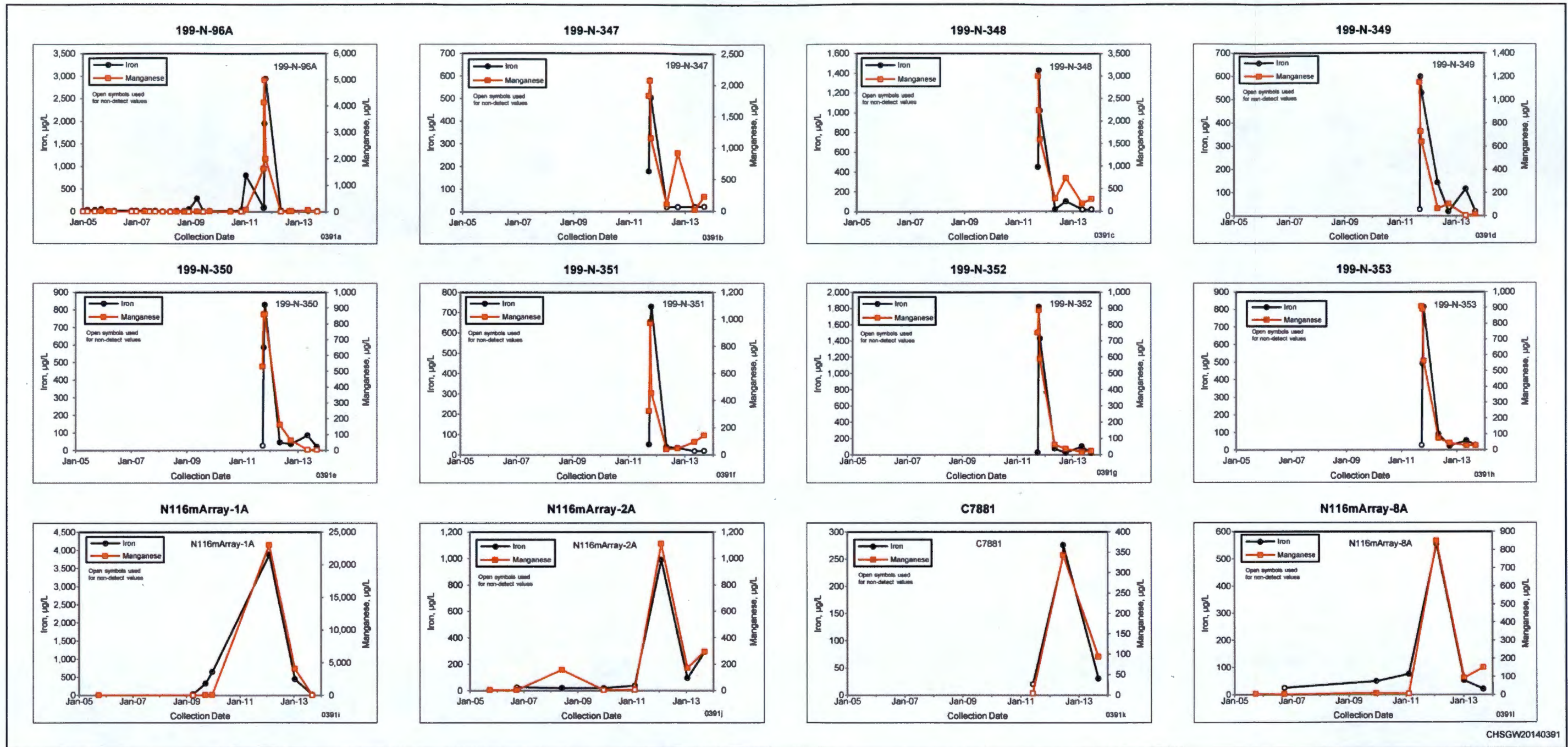
Only one baseline (pre-injection) sample was collected at the seven performance monitoring wells installed in 2010 for the upriver and downriver segments. All seven wells are screened in the deeper zone. The upriver wells were sampled during low water conditions in early April 2010 (water table elevation of 117.3 m); the downriver wells were sampled during higher water conditions in late July 2010 (water table elevation of 118.7 m). However post-treatment concentrations remain significantly lower than pre-treatment concentrations in six of these wells. In the seventh, the pre-injection and fall 2013 samples were less than the DWS for strontium-90.

- Temporary Increases. The injection of the apatite treatment solution caused temporary concentration increases in groundwater primarily of the divalent transition metals (e.g., cadmium, zinc, lead, and manganese). These increases reflect the temporary desorption of metals from the sediment in contact with the treatment solution, which has a significantly higher ionic strength than groundwater. The metals and anion concentrations reverted to background concentrations in less than six months (Figure 3-19).

Temporary increases in gross beta activity were observed immediately following the injections in 2008 and 2011 (Section 3.1.6). The increases were higher in 2008, when solutions were injected in the pre-treated area with higher strontium-90 concentrations. However, gross beta activity reverted to baseline within a couple of months following both injections of high concentration formulations. The similar trends suggest that injecting the high concentration formulation in untreated sediment did not result in a greater release of gross beta (or strontium-90) to groundwater or the river.

- Summary. Given the variability within the hydrogeologic and geochemical systems and in the volume of apatite solution injected into each well in 2011, it appears that injecting the high concentration formulation into untreated sediment is an effective approach for emplacing the apatite and that pre-treatment with the low concentration formulation does not improve the emplacement of apatite or reduce the transient release of metals and anions and increase in gross beta activity immediately following injection.

Note: The strontium-90 concentrations at the performance monitoring wells in the original barrier segment in 2010 (two years after upgradient injections) were compared to the concentrations at the performance monitoring wells in the upriver and downriver barrier segments in 2013 (two years after upgradient injections). Concentrations in performance monitoring wells in the original barrier segment, which are screened across both the shallow and deep zones, have fluctuated between August 2010 and fall 2013. In fall 2013, the percent reduction in strontium-90 concentration ranged from 73 to 93 percent. In fall 2013, the upriver and downriver performance monitoring wells, which are screened across the deep zone, showed reductions in strontium-90 concentrations generally ranging from 71 to 98 percent.



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Figure 3-19. Iron and Manganese Trends in Upriver and Downriver Performance Monitoring Wells and Aquifer Tubes

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3. Test the new well design installed under DOE/RL-2009-32 to evaluate the adequacy of injection solution delivery to the target zone.

The adequacy of injection solution delivery to the target zone (i.e., shallow or deep screened interval) was estimated based on the elevation of the water table in the downgradient performance monitoring wells during the injection and seven day reaction period. As discussed in Section 3.1.5, it appears that the injections may have resulted in the emplacement of at least 40 to 50 percent of the available apatite in the lower portion of the shallow screened intervals in upriver wells and more than 50 percent in the full thickness of the shallow screened intervals in downriver wells. The available apatite varies based on the injection volume delivered to each well. Delivery of the solutions to the shallow zone would have been improved had the injections occurred during higher water elevations. It appears that the injections resulted in the emplacement of apatite throughout the deep screened intervals; the amount of apatite emplaced varies with the volume injected.

Monitoring was not conducted in injection wells to evaluate the lateral distribution of injection fluids. The adequacy of the injection solution delivery laterally within the target zones was estimated based on the volume of solution injected, the saturated length of the screened interval, and assuming an average aquifer field porosity of 20 percent (Section 2.3 of PNNL-17429).

4. Test and optimize operation of the new injection system to verify that the system can deliver the designed injection solution flow volume at multiple well locations.

Although each new injection system was able to deliver approximately 1,363,000 L (360,000 gal) total during each phase of injections, and although each system injected into six wells simultaneously, not every well received the minimum design volume of 227,000 L (60,000 gal). Injection of apatite-forming solution continued at each skid until the total volume (nominally 1,363,000 L [360,000 gal]) was depleted. Data are not available to evaluate whether controlling the flow to individual wells during the injections would have reduced the variability in the volumes (e.g., by stopping the flow to wells that had received 227,000 L [60,000 gal] of solution).

5. Determine whether the new well design and injection system can complete chemical injections at various river stages, thereby eliminating the need for injections during specific river levels.

The 2011 injections were performed independent of river stage. All of the injections occurred during relatively low water table elevations.

Because all of the shallow wells were injected simultaneously, and all of the deep wells were injected simultaneously, it is likely that none of the injections achieved the 4.6 m (15 ft) lateral radius of influence needed to emplace apatite solutions throughout the 9.1 m (30 ft) lateral areas between the shallow injection wells and the 9.1 m (30 ft) lateral areas between the deep injection wells. As shown by monitoring during simultaneous injections into closely spaced wells, injections at adjacent wells hydraulically interfere with each other (Section 7.2 of PNNL-17429). Injection of apatite solution displaces groundwater in front of the apatite solution plume. As a result, the adjacent apatite plumes do not meet laterally because they are separated by displaced groundwater. The apatite-solutions form ellipsoids that are elongated in the downgradient direction. The superposition of adjacent injection mounds drives the reagent laterally away (upgradient or downgradient from the wells). Injection wells that received lower volumes of solution would be expected to have achieved a shorter, and/or discontinuous, radius of influence.

Based on the water level monitoring at performance monitoring wells during the shallow well injections, water levels were not at the top of the shallow screens and apatite was likely not emplaced through the entire vertical extent of the screened intervals in these wells. The vertical extent of apatite

emplacement would have been improved if injections in the shallow wells had been conducted during higher water table elevations. Apatite was emplaced through the entire vertical extent of the screened intervals in the deep wells during lower water table elevations. However, data are not available to evaluate whether injecting the deep wells during higher water table elevations would have reduced the effectiveness of apatite emplacement.

6. Evaluate that PRB can achieve up to 90 percent reduction in strontium-90 flux to the river.

Two years after the 2011 injections, in fall 2013, strontium-90 concentrations in the performance monitoring wells have been reduced by 71 to 98 percent in the three upriver wells in which the pre-injection concentration exceeded the DWS (8 pCi/L) (Table 3-11). In the fourth upriver well, the initial and fall 2013 strontium-90 concentrations were less than the DWS. Strontium-90 concentrations in downriver performance monitoring wells have been reduced by 87 to 97 percent. Results of future monitoring will be used to evaluate the long-term reduction in strontium-90 concentrations in groundwater reaching the river.

In fall 2013, strontium-90 concentrations in upriver aquifer tubes 116mArray-1A and 116mArray-2A had been reduced from 64 pCi/L to nondetect and from 360 to 18 pCi/L, respectively. In downriver aquifer tubes C7881 and 116mArray-8A, strontium-90 concentrations had been reduced from 350 to 42 pCi/L and from 47 to 1.1 pCi/L, respectively.

7. Further test the impact the high concentration calcium-citrate-phosphate solution has on the release of strontium-90 and other metals from previously untreated sediments to groundwater.

The apatite forming solution contains citrate and has a high ionic strength, much greater than that of groundwater, which cause a short-term release of strontium-90 and other trace metals normally sorbed to sediment. Following the injections in 2011, aluminum, chloride, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, strontium, and zinc exceeded their associated drinking water or water quality levels in some of the wells within the apatite treatment zone (Section 9.2.5.1 of DOE/RL-2012-15). Concentrations typically returned to pre-treatment levels within one month to one year, based on the monitoring frequency and constituent selection during the monitoring.

Evaluation of concentration data collected over the next few years will be used to determine longer-term concentration trends of strontium-90 and other metals and whether the 90 percent reduction of strontium-90 concentrations has occurred in the wells monitoring the upriver and downriver segments of the barrier. Further monitoring will also validate the transient release and return of metals and other constituent concentrations to natural background conditions.

8. Test the effectiveness of injecting adjacent shallow wells simultaneously and of injecting adjacent deep wells simultaneously.

As implemented in 2011, injections of apatite-forming solutions occurred simultaneously in adjacent wells (i.e., in all of the upriver deep wells; then in all of the upriver shallow wells; then in all of the downriver deep wells; and then in all of the downriver shallow wells). Based on this approach, no wells were available for monitoring between the injection wells to evaluate the arrival of chemicals and to assess the lateral radius of influence. Based on previous observations, injecting adjacent wells also caused hydraulic interferences from mounding that can reduce the lateral coverage in the overlap zones (Section 7.2 of PNNL-17429).

3.4 Quality Assurance/Quality Control

In accordance with the DOS (Section 5.2 of DOE/RL-2010-29), a quality assurance inspection was conducted on the apatite injection systems following fabrication. Each system passed a pressure/leak test, documented in pressure/leak test reports. Instrumentation (e.g., flowmeters and pumps) was verified as being the correct manufacturer and model, accompanied by factory calibration certificates, as appropriate. Exposed fasteners were inspected to confirm that none were suspect/counterfeit items.

Data validation was performed for the analytical data, in accordance with the DOS (Section 8.1 of DOE/RL-2010-29). Level C validation, which is a review of the quality control data, was performed on at least 5 percent of the data by matrix and analyte group. The matrix of the validation samples was water, and the analyte groups were radionuclides, semivolatile organics (TPH-diesel), inorganics (metals), and general chemistry (anions). Analytical data were available for the samples of river water and injection chemicals collected during the injections and the samples of groundwater collected following the injections at monitoring wells and aquifer tubes. The data validation found no deficiencies (major or minor) in any of the four analyte groups. No data reporting qualifiers were applied to the data based on the data validation. The data validation report is provided in Appendix H. Conclusions and Recommendations

The following conclusions and recommendations are based on the evaluation of the injections of apatite solutions in 2011.

3.5 Timing of Injections Relative to Water Table Elevation

During the injections into the upriver shallow wells, the ambient water level remained below the screened intervals of the shallow injection wells during the injections and the following 7-day apatite reaction period. As a result of temporary mounding of the water table in response to the injections, the lower portion of the screened intervals was saturated during part of this time, and apatite would have formed using the calcium released from the citrate. It is possible that 25 percent of the potential apatite mass was emplaced in the lower portion of the shallow aquifer zone. The mass of apatite would vary from well to well based on the volume of the injected solution.

During the injections into the downriver shallow wells, the ambient water level remained within the screened intervals of the shallow injection wells during the injections and the 7-day apatite reaction period. As a result of temporary mounding of the water table in response to the injections, the entire portion of the screened interval was saturated during part of this time and apatite would have formed using the calcium released from the citrate. It is possible that almost half of the potential apatite mass was emplaced in the full thickness of the shallow aquifer zone. The mass of apatite would vary from well to well based on the volume of the injected solution.

During the injections into the upriver and downriver deep wells, the ambient water level remained above the screened intervals of the deep injection wells during the injections and the 7-day apatite reaction period. Artificially elevated water levels above the ambient water level were recorded in downgradient monitoring wells as a result of the injections. It is likely, therefore, that apatite was emplaced in the deeper portion of the aquifer throughout the screened intervals and potentially extending up to the water table at these locations. The mass of apatite would vary from well to well based on the volume of the injected solution.

During the groundwater mounding resulting from the deep upriver injections, it is possible that apatite also was formed in the shallow aquifer zone during the injections to deep wells that received sufficient volumes of reagents.

As concluded based on injections in the central (original) segment of the barrier, injection into the shallow aquifer wells during high river stage does not have to rely on mounding to treat the upper aquifer zone, and is more effective than at low river stage (PNNL-19572). As concluded based on injections in the central (original) segment of the barrier, injection into the deep aquifer wells is more effective during low river stage (PNNL-19572). While the 2011 injections during relatively low water appear to have successfully treated the deep aquifer zone, data from the 2011 injections are not available to support the conclusion that injecting during high water is less optimal for this depth. If a thick zone above the deep screen is saturated, the pressure pulse from the injection will cause some of the injected solution to move upward, in addition to radially, leaving less of the apatite-forming chemicals in the target zone. However, the upward movement would be limited because the horizontal transmissivity is typically much higher than the vertical transmissivity.

Recommendation: Inject into the shallow aquifer wells during high river stage. Inject into the deeper aquifer wells at low river stage. Minimize injection of apatite-forming solution into wells with partially unsaturated screened intervals.

3.6 Injection Well Timing and Order of Treatment

During the 2011 injections, all of the upriver deep wells were injected simultaneously, followed 4 days later by all of the upriver shallow wells. Similarly, all of the downriver deep wells were injected simultaneously, followed 2.5 hours later by all of the downriver shallow wells. Injecting all of the upriver deep wells at the same time did not allow monitoring at intervening deep wells within the barrier well network to evaluate the distribution of the apatite solution and radius of apatite emplacement around the injection points. The same inability to monitor intervening wells of the same target depth was true during all of the injections.

Recommendation: Design the sequence of injection wells to allow monitoring of injection solution distribution laterally between the barrier injection wells during injections. Design the sequence of injection wells to minimize hydraulic interference of injected solution volumes and maximize the lateral distribution of the injection solutions. Monitor adjacent apatite barrier network wells during injections (field parameters, especially conductivity, and phosphate) to determine rate and radial extent of dispersion. If feasible, inject in every third well simultaneously at a given target depth. Inject apatite-forming solution in wells adjacent to injected wells only after the 7-day reaction period has elapsed. Conduct numerical simulations using a site-specific apatite PRB model to evaluate the distribution of the apatite-forming solutions to support planning for injections of remaining untreated portions of the PRB. Data from previous injections could be used to calibrate the model.

3.7 Injection Volume and Rate

The volume of apatite solution injected into each upriver deep well ranged from 49,693 to 567,078 L (13,129 to 149,822 gal). The volume of apatite solution injected into each upriver shallow well ranged from 43,153 to 347,898 L (11,401 to 91,915 gal). The volume of apatite solution injected into each downriver deep well ranged from 51,764 to 389,499 L (13,676 to 102,906 gal). The volume of apatite solution injected into each downriver shallow well ranged from 95 to 509,192 L (25 to 134,529 gal). All of the injection wells on a skid were used for injection until the entire volume of apatite-forming solution delivered to the skid had been depleted. The injection wells received differing volumes of solution as a result of subsurface heterogeneities.

Recommendation. During injection operations, discontinue or reduce injections in wells that have received the target injection volume, after monitoring indicates adequate lateral distribution of solution, and continue injecting remaining wells until the target volume (e.g., 227,000 L [60,000 gal]) has been

injected. PNNL-19572 (Sections 5.0 and 5.1) recommended maintaining the injection volume for shallow wells at 227,000 L (60,000 gal) and increasing the injection volume for deep (Ringold) wells up to 454,000 L (120,000 gal) because of loss of injection solution to the Hanford formation. The higher volume recommended for the deeper zone could be reduced based on the hydrogeologic conditions at each well or part of the barrier (i.e., based on the thickness and hydraulic conductivity of the Hanford formation). The adequacy of the reduced volume would need to be confirmed based on results from monitoring adjacent wells during an injection. For future injections, base the volumes injected in the deeper zones on site-specific conditions. Prior to use for additional injections, test and repair, as needed, the totalizers and other skid instrumentation.

3.8 Post-Injection Performance Monitoring

Post-injection performance monitoring was conducted in downgradient performance monitoring wells and aquifer tubes three times within the 5 weeks following injections. The samples were analyzed for gross beta, anions, cations and metals, and, in upriver wells only, TPH-diesel.

Recommendation: During post-injection monitoring, consider monitoring for gross beta (a less expensive surrogate for strontium-90) in injection wells to increase the spatial resolution of the data.

3.9 Operational Performance

Sufficient vertical placement of apatite may not have been achieved in the shallow aquifer zone at the barrier because of the low water levels, the inability to maintain the artificial injection mound over a sufficient length of time to allow formation of the entire potential mass of apatite, and the injection of low volumes of solution at many wells. It is unlikely that apatite emplacement in the deep aquifer wells at the barrier formed a continuous treatment zone (i.e., the radii of emplacement overlapped) because of hydraulic interference between simultaneous injections in adjacent wells.

Overall, the reduction in strontium-90 concentrations ranged from 71 to 98 percent in September 2013, two years after injections were completed, at seven of the eight downgradient performance monitoring wells. At the eighth well, the pre-injection and September 2013 strontium-90 concentrations were less than the DWS (8 pCi/L).

Recommendation: Continue to collect performance monitoring data at downgradient monitoring wells to evaluate the apatite emplacement and its long-term ability to reduce strontium-90 concentrations reaching the river.

It is recommended that core samples not be collected to evaluate the vertical and radial extent of apatite formation within the most recently placed portions of the barrier. The DOS specified that continuous core samples would be collected after a minimum of one year following completion of the injections if the groundwater and aquifer tube monitoring data show a 90 percent reduction in strontium-90 flux to the river and, if no considerable reduction is shown, re-injection would be implemented and soil cores would not be collected (Section 6.5 of DOE/RL-2010-29). Core samples would be used to determine the vertical and radial extent of calcium-citrate-phosphate injection into the soil column and to determine the degree of apatite formation. However, a good use of core samples is to confirm the adequacy of the design when all of the design criteria have been met. Because of the uncertainties in the 2011 apatite emplacement operations (e.g., low volumes in many wells, low river stage for shallow zone injections, and simultaneous adjacent injections with no adjacent injection monitoring), it would be difficult to determine whether the core results could be attributed to the design or implementation. The percent reduction of strontium-90 in the performance monitoring wells during the first two years is high. If there is early

breakthrough or a lower percent reduction of strontium-90 in the performance monitoring wells in the future, re-injection can be considered.

3.10 Adequacy of Apatite Emplacement

The target apatite concentration was not achieved in 16 injection wells. At some of these injection wells, the adjacent upriver and downriver injection wells received sufficient phosphate to form the target apatite concentration. But at two locations, adjacent injection wells did not receive sufficient phosphate: from Well 199-N-215 to Well 199-N-217 and from Well 199-N-239 to Well 199-N-244. Injection Wells 199-N-215 through 199-N-217 appear to be in a low flow zone with low strontium-90 concentrations, and the strontium-90 concentration in downgradient monitoring Well 199-N-347 is less than the DWS. Strontium-90 concentrations in monitoring Wells 199-N-350 and 199-N-351, downgradient of injection Wells 199-N-239 through 199-N-244, show 88 and 87 percent reductions of strontium-90, respectively, in the near term. However, these reductions may not be sustained over the long term because the phosphate injected in barrier Wells 199-N-239 through 199-N-244 was lower than the target concentration. This portion of the barrier may require future re-injection for long-term sequestration of strontium.

Recommendation: Improvements in the future apatite barrier treatment could be realized by the following actions:

- Timing the shallow injections for when the water table is higher, typically during spring or early summer, would improve the placement of apatite in the shallower aquifer zone.
- Injecting into the network in a staggered pattern would allow monitoring between injection wells for assessing the lateral extent of treatment and improving apatite placement along the barrier axis.
- Adjusting or turning off wells during treatment that have received the full volume of treatment would allow the remaining volume to be targeted into the wells with the least treatment volume.

3.11 Future Baseline Sampling

Baseline samples were collected from the apatite barrier network wells and downgradient performance monitoring wells once in 2010.

Recommendations:

- Monitor performance monitoring wells downgradient of the apatite barrier network wells that have not yet been injected with apatite solutions (Table 4-1). Monitoring of these wells prior to injection of apatite solutions in the barrier wells will provide the needed pre-treatment baseline concentration data for metals and strontium-90 (or gross beta) to evaluate barrier performance.
- Monitor apatite barrier network wells that have not yet been injected with apatite solutions. Monitoring of these wells prior to injection of apatite solutions will provide the needed pre-treatment baseline concentration data for metals and strontium-90 (or gross beta) to evaluate apatite solution emplacement.
- Monitor adjacent pairs of wells that have not yet been injected with apatite solutions. Monitoring of these wells prior to injection of apatite solutions will enhance understanding of groundwater and contaminant movement and impact, and river influence across and through the shallow and deep hydraulic zones.
- Monitor aquifer tubes downgradient of the apatite barrier network wells that have not yet been injected with apatite solutions. Monitoring of these aquifer tubes prior to injection of apatite solutions

in the barrier wells will provide the needed pre-treatment baseline concentration data for metals and strontium-90 (or gross beta). Aquifer tubes in need of repair (e.g., C6472 and N116mArray-8.5A) should be repaired or replaced to support apatite barrier monitoring.

- At all of these monitoring locations, sample at multiple river stages for strontium-90 (or gross beta) to establish minimum and maximum pre-injection concentrations. Monitor for other constituents annually for water quality information.

Table 3-12. Groundwater Monitoring Wells, Apatite Barrier Network Wells, and Aquifer Tubes Identified for Baseline Monitoring

Groundwater Monitoring Wells			
199-N-173	199-N-357	199-N-362	199-N-367
199-N-346	199-N-358	199-N-363	199-N-92A
199-N-354	199-N-359	199-N-364	
199-N-355	199-N-360	199-N-365	
199-N-356	199-N-361	199-N-366	
Apatite Barrier Network Wells			
199-N-136 (Shallow and Deep)	199-N-229 (Deep)	199-N-280 (Deep)	199-N-332 (Deep)
199-N-159 (Deep)	199-N-230 (Shallow)	199-N-281 (Shallow)	199-N-333 (Shallow)
199-N-200 (Shallow)	199-N-247 (Shallow)	199-N-297 (Shallow)	199-N-342 (Deep)
199-N-201 (Deep)	199-N-248 (Deep)	199-N-298 (Deep)	199-N-343 (Shallow)
199-N-210 (Shallow)	199-N-268 (Deep)	199-N-315 (Shallow)	
199-N-211 (Deep)	199-N-269 (Shallow)	199-N-316 (Deep)	
Aquifer Tubes			
C6132	C6324	N116mArray-9A	N116mArray-11A
C6136	N116mArray-0A	N116mArray-10A	N116mArray-15A

3.12 Performance Monitoring Wells

All of the performance monitoring wells installed along the extended apatite barrier are screened in the deeper zone. The highest strontium-90 soil concentrations are near the average water table, and strontium-90 soil concentrations also are found above the average water table. When groundwater increases in elevation during high or average river stage, it can mobilize strontium-90 contamination. When the river stage decreases and the groundwater flow is toward the river, the groundwater will flow through the deep zone. However, some groundwater may flow in zones above the deep interval.

Recommendation: Evaluate whether concentrations in groundwater sampled from the deep zone in performance monitoring wells would differ significantly from concentrations in groundwater flowing

above these zone. Evaluate the need for additional performance monitoring wells screened over a longer interval that includes shallower zones.

4 References

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Appendix A

Pre-Injection Analytical Data for Apatite Permeable Reactive Barrier Injection and Monitoring Wells Installed in 2009 and 2010

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This appendix provides all of the analytical and field results for groundwater samples collected in 2010 from the 100-N apatite permeable reactive barrier injection and monitoring wells that were installed in 2009 and 2010 to extend the length of the barrier from 91 m (300 ft) to 762 m (2,500 ft). These results are pre-injection concentrations.

All of the groundwater data presented in this appendix are provided on the accompanying CD as Supporting Information A-1.

The data are stored in the Hanford Environmental Information System (HEIS) database, and users also may retrieve the data via the internet through the DOE Environmental Dashboard Application available at: <http://environet.hanford.gov/EDA/>.

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Appendix B

100-NR-2 Operable Unit Apatite Barrier Injection System Design Description

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Terms

AFD	adjustable frequency drive
bgs	below ground surface
DOS	design optimization study
FIT	flow indicating transmitter
FQI	flow indicating totalizer
OU	operable unit
P&ID	process and instrument diagram
PRB	permeable reactive barrier
PVC	polyvinyl chloride
RAO	remedial action objective
ROD	record of decision
SDD	system design description

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B1 Introduction

This 100-NR-2 Operable Unit (OU) apatite barrier injection system design description (SDD) has been prepared to document the following features of the chemical injection skid:

- Functions
- Design requirements
- Physical characteristics
- Operating principles
- Equipment list
- Project drawing list

This SDD should be used in conjunction with the system process and instrumentation diagrams (P&IDs), design specifications, and other design drawings, as appropriate.

B1.1 Background

Activities to reduce the flux of strontium-90 to the Columbia River from past-practice liquid waste disposal sites have been underway since the early 1990s in the 100-N Area at the Hanford Site. Termination of all liquid discharges to the ground by 1993 was a major step toward meeting this goal. However, residual strontium-90 adsorbed on aquifer and periodically rewetted zone sediments beneath the liquid waste disposal sites and extending beneath the nearshore riverbed remains as a continuing source of contamination to groundwater and the Columbia River.

Following an evaluation of potential strontium-90 treatment technologies and their applicability under 100-NR-2 OU hydrogeological conditions, the U.S. Department of Energy, U.S. Environmental Protection Agency, and Washington State Department of Ecology agreed that the long-term strategy for groundwater remediation at the 100-N Area should include apatite sequestration as the primary treatment technology (DOE/RL-2006-20, *The Second CERCLA Five-Year Review Report for the Hanford Site*). This agreement was based on results from an evaluation of remedial alternatives that identified the apatite permeable reactive barrier (PRB) technology as the approach showing the greatest promise for reducing strontium-90 flux to the Columbia River at a reasonable cost. The Interim Action Record of Decision (ROD), as amended (EPA, 2010, *U.S. Department of Energy, 100-NR-1 and NR-2 Operable Units Hanford Site – 100 Area Benton Country, Washington Amended Record of Decision, Decision Summary and Responsiveness Summary*), replaces the strontium-90 groundwater pump and treat system with a subsurface PRB comprised of apatite injected into both the saturated zone and the vadose zone.

As described in PNNL-16891, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO₄ Solution Injection and Sr-90 Immobilization in 100-N Sediments*, the method of emplacing apatite in subsurface sediments at the 100-N Area involves injecting an aqueous solution containing a calcium-citrate complex and sodium phosphate. Citrate keeps the calcium in solution long enough (days) to migrate into the subsurface, a solution containing only calcium and phosphate will rapidly precipitate, forming mono- and di-calcium phosphate. The relatively slow biodegradation of the calcium-citrate complex (days) allows sufficient time for injection and transport of the reagents to the areas of the aquifer where treatment is required. As calcium-citrate is degraded, the free calcium and phosphate combine within a week to form amorphous apatite that, in a few weeks, transforms into crystalline apatite.

B1.2 System Identification

The scope of this SDD covers the 100-NR-2 OU apatite barrier injection system for injecting apatite-forming chemicals into the aquifer to emplace apatite into the saturated sediments to form the PRB for strontium sequestration at the 100-N Area of the Hanford Site.

B2 General Overview

The following sections describe the primary functions associated with the 100-NR-2 OU apatite barrier injection system and the overall classification of the system and its components in order to establish a foundation for understanding the requirements and bases subsequently presented in Chapter B3.

B2.1 System Functions

The 100-NR-2 OU apatite barrier injection system is designed to address the following remedial action objectives (RAOs) described in the Interim Action ROD (EPA, 2010):

- Protect the Columbia River from adverse impacts from the 100-NR-2 OU groundwater so that designated beneficial uses of the Columbia River are maintained. Protect associated potential human and ecological receptors using the river from exposure to radioactive and nonradioactive contaminants present in the unconfined aquifer. Protection will be achieved by limiting exposure pathways, reducing or removing contaminant sources, controlling groundwater movement, or reducing concentrations of contaminants in the unconfined aquifer.
- Protect the unconfined aquifer by implementing remedial actions that reduce concentrations of radioactive and nonradioactive contaminants present in the unconfined aquifer.
- Obtain information to evaluate technologies for strontium-90 removal, and evaluate ecological receptor impacts from contaminated groundwater.¹
- Prevent destruction of sensitive wildlife habitat. Minimize the disruption of cultural resources and wildlife habitat in general, and prevent adverse impacts to cultural resources and threatened or endangered species.

In addition to the preceding RAOs, the design optimization study (DOS) (DOE/RL-2010-29, *Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit*) defines the following objectives:

1. Refine application of the high-concentration calcium-citrate-phosphate solution over a larger scale.

Refine the application of the high-concentration calcium-citrate-phosphate solution through testing the well design, injection equipment, monitoring well sampling, and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions.

2. Test the effectiveness of high-concentration calcium-citrate-phosphate injection in previously untested sediment to compare with areas that received sequential injections of low- then high-concentration calcium-citrate-phosphate injections.

Effectiveness will be demonstrated through long-term monitoring of wells and aquifer tubes as explained in Section 3 of the DOS (DOE/RL-2010-29) through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking of transient effects of increased metals and anions.

¹ Note that this RAO was achieved with the issuance of FH-0403540, "Transmittal of the Draft Letter Report, Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit," and DOE/RL-2006-26, *Aquatic and Riparian Receptor Impact Information for the 100-NR-2 Groundwater Operable Unit*.

3. Test the new well design installed under DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*, to evaluate the adequacy of injection solution delivery to the target zone.

The new well design will be evaluated through monitoring of groundwater and aquifer tubes as described in Section 3 of the DOS (DOE/RL-2010-29) through collection of field conductivity measurements in conjunction with groundwater sampling for phosphate.

4. Test and optimize operation of the new injection system to verify that the system can deliver the designed injection solution flow volume at multiple well locations. Determine whether the new well design and injection system can complete chemical injections at various river stages, thereby eliminating the need for injections during specific river levels.

This will be evaluated by performing injections independent of river stage and collecting field conductivity measurements in conjunction with groundwater sampling for phosphate to determine the treatment area achieved.

5. Evaluate that PRB can achieve up to a 90 percent reduction in strontium-90 flux to the river.

This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and by tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4 [of the DOS (DOE/RL-2010-29)].

6. Further test the impact the high-concentration calcium-citrate-phosphate solution has on the release of strontium-90 and other metals from previously untreated sediments to groundwater.

This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4 [of the DOS].

The primary function of the 100-NR-2 OU apatite barrier injection system is to protect the Columbia River from adverse impacts from the 100-NR-2 OU groundwater so that designated beneficial uses of the Columbia River are maintained. This is accomplished by injection of apatite-forming chemicals into existing PRB injection wells to emplace apatite into the saturated sediments to sequester strontium contamination in the groundwater and reduce the strontium-90 contamination flux to the river. The primary objective of the 100-NR-2 OU apatite barrier injection system, and the primary functions necessary to achieve it, are represented graphically in Figure B-1.

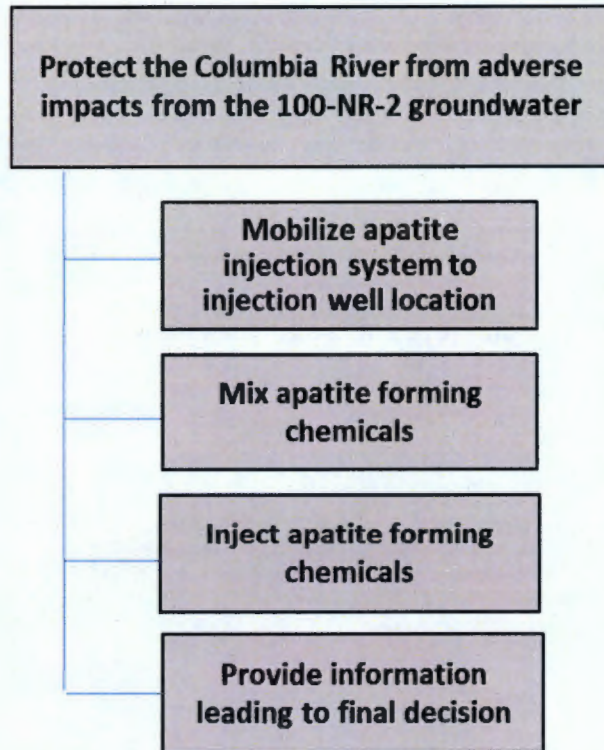


Figure B-1. General Functions of the 100-NR-2 OU Apatite Barrier Injection System

B2.2 System Classifications

The 100-NR-2 OU apatite barrier injection system has been categorized as less than Hazard Category 3 (HC-3). This includes all facilities and subsystems associated with the 100-NR-2 OU apatite barrier injection system. As such, all the structures, systems, and components for the 100-NR-2 OU apatite barrier injection system will be safety class GS.

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B3 System Requirements

The following subsections identify requirements imposed on the 100-NR-2 OU apatite barrier injection system and its components and present the bases for these criteria.

B3.1 Treatment Requirements

The performance objective for the apatite barrier injection system is to achieve a 90 percent reduction in strontium-90 flux to the Columbia River within 5 years of completing all apatite injections.

B3.2 Instrumentation and Control Requirements

- The apatite injection equipment is designed to be portable so that it can be moved to different locations for treating up to 762 m (2,500 ft) of the Columbia River bank.
- Each injection trailer was designed to pump up to 1,136 lpm (300 gpm) of water from the Columbia River to treat up to six wells concurrently at an injection rate of 76 to 189 lpm (20 to 50 gpm).
- The equipment is designed to blend apatite-forming chemicals with water at a 1:10 ratio.
- Adjustable frequency drives (AFDs) are used to control the flow of chemicals and river water to each injection trailer.

B3.3 Interface Requirements

- Access roads – Existing roads will be used, as practicable, in lieu of developing new roads. Where new roads are required, their layout will minimize disturbance of the site.
- Electrical – All electrical utilities will be provided by portable generators.
- Analytical services.
- Other – No connections to raw water, sanitary water, or sewer systems are required.

B3.4 Codes, Standards, and Regulations

- ANSI/ASME, 2008, *Process Piping*
- NFPA 70, *National Electrical Code*
- NFPA 1, *Fire Code*, Chapter 60, "Fire Safety, Hazardous Materials"

B3.5 Engineering Disciplinary Requirements

Design criteria for engineering disciplines are specified in apatite barrier injection system released drawings:

- Civil/structural – H-1-91580-1
- Piping – H-1-91586-1
- Electrical/control – H-1-91593-1, H-1-91595-1, H-1-91600-1, and H-1-91601-1

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B4 Process Components and Design Features

Each apatite barrier injection system consists of the following equipment:

- Submersible pump placed in the Columbia River to supply water to dilute the two chemical solutions
- Chemical feed tanks located on top of the bluff above the river
- Skid containing equipment for blending chemical solutions and river water at carefully controlled ratios and flow rates
- Generator to supply electrical power
- Electrical distribution system
- Interconnecting hoses
- Injection wells

The two chemical mixing skids are similar in that each contains an inlet filter for river water, an electrical distribution and process control system, flowmeters for monitoring water and chemical flows, chemical feed pumps, and sample points as well as pressure gages, pressure regulators, and manual valves.

The two chemical solutions feed via 5 cm (2 in.) diameter clear, reinforced hose from portable storage tanks located on the bluff above the injection site to the chemical mix skids located on the shoreline road. Water pumps from the river through a 10 cm (4 in.) diameter chemical hose to the chemical mix skid, where it is filtered and then mixed with the chemical solutions to obtain the correct concentration for injection. Each skid contains three parallel filters. The filters are sized so that only two need to be online at any given time. This allows operations to continue during filter changes. AFDs on the river water pumps and chemical pumps are set so that the correct ratio of water to chemicals is maintained. The desired river water flow is set on the river pump AFD. Then the chemical pump AFDs will automatically adjust the chemical solution flow to maintain the correct ratio. The blended stream flows from the chemical mix skids through 5 cm (2 in.) diameter hoses to the injection wells. A splitter installed on the chemical mix skids allows simultaneous injection of chemicals in up to six wells at one time from one skid.

Technical data and vendor model numbers for the two chemical injection skid components identified as follows are listed on drawings H-1-91586 and H-1-91588.

B4.1 Dilution Water Supply System

Dilution water for the apatite barrier injection system is supplied by a submersible pump located in the Columbia River at a distance of 15 to 30 m (50 to 100 ft) offshore. The pump has a fish screen attached to the inlet. The pump and screen are mounted on a 1 by 2.4 m (3 by 8 ft) angle iron framework covered by a sheet of 1 cm (3/8 in.) aluminum. A swivel hoist ring is attached near the front and rear corners on one side of the framework so that the pump assembly can be rigged and lowered into the river from a boat. A 10 cm (4 in.) diameter chemical hose connects to a cam-and-groove fitting on the pump outlet and extends from the pump to the shore to connect the pump to the chemical skid located on the riverbank. A submersible power cable is hardwired to the pump motor with the other end connected to the chemical injection skid power panel.

B4.1.1 River (Dilution) Water Pump

The submersible pump used for pumping river water for dilution of chemical feed will have a range of 0 to 1,136 lpm (0 to 300 gpm).

B4.1.2 Fish Screen

The fish screen is a Pump-Rite model L250 made by Pacific Ag Systems, or equivalent. It has a 25 cm (10 in.) diameter by 152 cm (60 in.) long screen with flow capacity of 946 lpm (250 gpm). The screen meets the 0.06 m/s (0.2 ft/s) approach velocity criterion of the U.S. Bureau of Reclamation.

B4.2 Chemical Feed System

The apatite-forming chemicals are delivered to the site by tank trucks and transferred into vendor-supplied portable feed tanks located on top of the bluff above the Columbia River. There are separate feed tanks for calcium-citrate solutions and phosphate solutions. There is also one water tank for flushing equipment. All of the phosphate solution feed tanks are connected to a common manifold. Solution can be fed from individual tanks or from all of the tanks at the same time. All of the phosphate solution needed for an injection is made up offsite and transferred into the chemical feed tanks prior to the start of the injection. Since the calcium-citrate solution is subject to biodegradation, the solution is made up and delivered to the site during the course of the injection. The four calcium-citrate feed tanks are set up as two banks to allow chemicals to feed from one bank of tanks while the other bank is filled.

B4.2.1 Chemical Feed Hose

The chemical solutions drain from the tanks to the injection trailer by 5 cm (2 in.) diameter reinforced hose. The hoses consist of a series of 15 m (50 ft) sections with cam-and-groove quick-disconnect fittings on both ends so that they can be disassembled and reassembled when the equipment is moved.

B4.2.2 Chemical Feed Pumps

Each trailer contains two chemical feed pumps. The chemical feed pumps control the flow of chemicals to the chemical blend system.

B4.2.3 Pressure Control Valve

A pressure control valve is located upstream from each chemical feed pump to limit the pressure to the pump caused by the head of fluid between the chemical tanks and the injection trailer.

B4.2.4 Flow and Pressure Measurement

Flow indicating transmitters (FITs) are located downstream from the chemical pumps. The FITs have a range of 0 to 114 lpm (0 to 30 gpm). The FITs have a local display and send a signal to the corresponding pump AFD and to a remote indicator in the control panel. These FITs also have a totalizing function.

Pressure gages are located upstream and downstream of the pressure control valves and on the combined flow stream. Pressure gages are also located on the filter vessels upstream and downstream of the filter media.

B4.3 Chemical Blending System

The water from the dilution water feed pump in the river passes through a check valve and then through a filtration system and FIT before it is mixed with the apatite-forming chemicals.

B4.3.1 Filters

The filtration system consists of a bank of three parallel bag filters. The filters have a flow capacity of 833 lpm (220 gpm) each at a differential pressure of 15.2 kPa (2.2 psig) and operate with two filters online and one offline. This allows filter element replacement without shutting down the injection operation. The filter housings are 22 cm (8 5/8 in.) outer diameter by 84 cm (33 in.) high carbon steel vessels with pressure gages installed both upstream and downstream. The filters have upstream and downstream isolation valves as well as vent and drain valves.

B4.3.2 Water Flow Measurement

FITs are located upstream and downstream from where the river water and apatite-forming chemicals combine. The FITs have a range of 0 to 1,136 lpm (0 to 300 gpm). These FITs also have a totalizing function. The river water FIT has a local display and sends a signal to the river pump AFD and to a remote indicator in the control panel. The downstream FIT has a local display and sends a signal to a remote indicator in the control panel.

B4.3.3 Static Mixer

The static mixer, consisting of a helical mixing element, directs the flow of material radially toward the pipe walls and back to the center. Additional velocity reversal and flow division result from combining alternating right- and left-hand elements, increasing mixing efficiency.

B4.3.4 Electrical Power

Electrical power for each trailer is supplied by a 480 VAC portable generator with a disconnect switch located on an adjacent rack. A three-phase 480 V power cord is used to carry power from the disconnect rack to the trailer. The power cord has plugs on both ends to facilitate moving the equipment when needed.

B4.3.5 Control System

Flow control for the river pump and chemical pumps is provided by AFDs. A control panel mounted on the side of the trailer contains flow indicators for river water, chemicals, and combined flows. It also contains control knobs for adjusting the river water flow set point and the chemical-to-river water flow ratios. The AFDs are set so that the correct ratio of water to chemicals is maintained. The desired river water flow is set by adjusting the river pump AFD controller to obtain the desired flow as shown on the river water flow indicator. The desired chemical to water ratio is set on the chemical pump AFD controllers. The chemical pump AFDs then automatically adjust the chemical solution flow to maintain the correct ratio when the river water flow is changed.

B4.4 Chemical Injection System

After passing through the static mixer, the diluted chemical mix splits up into six streams, which allows the apatite-forming chemical mix to be injected into six wells simultaneously. A manual globe valve controls the flow to each well. Then the chemical mix passes through a flow indicating totalizer (FQI) and a block valve, leaves the trailer, and is routed through a 5 cm (2 in.) chemical hose to an injection well. The hoses connect to the trailer and well piping by cam-and-groove quick-disconnect fittings.

B4.4.1 Injection Flow Measurement and Control

FQIs with a range of 0 to 189 lpm (0 to 50 gpm) are located downstream from the injection line flow control valves to provide local indication. A pressure gage installed between the injection hose and the wellhead piping provides pressure indication at the wellheads. The pressure gage is installed in a pipe tee with a male cam-and-groove fitting on one end and a female cam-and-groove fitting on the other end.

B4.4.2 Injection Wells

Injection wells were constructed using 15 cm (6 in.) diameter polyvinyl chloride (PVC) screen and casing and are completed at depths of approximately 4.6 m (15 ft) below ground surface (bgs) for the shallow (Hanford formation) wells and 7.6 m (25 ft) bgs for the deep (Ringold Formation) wells. The well casing terminates just below ground surface. The wells are spaced 4.6 m (15 ft) apart with alternating 4.6 and 7.6 m (15 and 25 ft) depths. When not being used for injection, the wells are sealed.

B4.4.3 Injection Well Piping

The injection well piping is fabricated of 5 cm (2 in.) galvanized steel above the landing plate and 5 cm (2 in.) PVC below the landing plate. The lower 1.5 m (5 ft) of the injection piping is perforated with four rows of 0.15 m (0.5 in.) diameter holes spaced 15 cm (6 in.) apart and is capped at the bottom with a slip-on PVC cap. The injection piping is installed in the wells prior to the start of an injection and removed when the injection is completed. The injection piping was fabricated in two lengths: 4.4 m (14.5 ft) for installation in the 4.6 m (15 ft) deep wells and 7.5 m (24.5 ft) for installation in the 7.6 m (25 ft) deep wells.

B4.4.4 Injection Well Seals

The injection piping is sealed to the well piping at ground level with a Merrill Iron & Steel model WS600200 landing plate. The injection well piping is sealed above the well screen by an RST Instruments model P5-9 well packer. The packer is inflated with air to seal the annulus between the injection well piping and the well casing. The air is supplied by a portable compressor powered by an electric motor. The air is routed to the wells through a distribution manifold made of 0.6 cm (0.25 in.) Kynar® tubing and brass compression fittings. Isolation and vent valves are located on the line leading to each well packer.

B4.5 100-NR-2 OU Apatite Injection System Operations

Valve lineup, pre-startup checks, operation, and shutdown of the 100-NR-2 OU apatite barrier injection system are found in facility-specific operating procedures. A list of the apatite injection design drawings with their descriptions is provided in Table B-1.

Table B-1. Design Drawing List

Drawing Number/Sheet	Description
Civil/Structural	
H-1-91573-1	Apatite injection system drawing list
H-1-91574-1	Apatite injection system civil site plan (existing)
H-1-91574-2	Apatite injection system civil enlarged site plan (existing)
H-1-91575-1	Apatite injection system civil site plan
H-1-91576-1	Apatite injection system civil enlarged site plan – A
H-1-91577-1	Apatite injection system civil enlarged site plan – B
H-1-91578-1	Apatite injection system civil enlarged site plan – C (future)

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Drawing Number/Sheet	Description
H-1-91579 -1	Apatite injection system civil enlarged site plan – D (future)
H-1-91580-1	Apatite injection system structural plan and notes
H-1-91581 -1	Apatite injection system structural sections and details
H-1-91582-1	Apatite injection system structural sections and details
H-1-91583-1	Apatite injection system structural sections and details
H-1-91583-2	Apatite injection system structural sections and details
Piping	
H-1-91584-1	Apatite injection system P&ID injection trailer N1
H-1-91585-1	Apatite injection system P&ID injection trailer N2
H-1-91586-1	Apatite injection system mechanical injection trailer N1
H-1-91587-1	Apatite injection system mechanical trailer N1 sections
H-1-91588-1	Apatite injection system mechanical injection trailer N2
H-1-91589-1	Apatite injection system mechanical trailer N2 sections
Electrical/Control	
H-1-91592-1	Apatite injection system electrical typical site plan
H-1-91592-2	Apatite injection system electrical details
H-1-91593-1	Apatite injection system trailer N1 plans and details
H-1-91593-2	Apatite injection system trailer N1 plans and details
H-1-91593-3	Apatite injection system trailer N1 plans and details
H-1-91594-1	Apatite injection system one-line and panel board schedule trailer N1
H-1-91595-1	Apatite injection system trailer N2 plans and details
H-1-91595 -2	Apatite injection system trailer N2 plans and details
H-1-91595-3	Apatite injection system trailer N2 plans and details
H-1-91596-1	Apatite injection system one-line and panel board schedule trailer N2
H-1-91600-1	Apatite injection system control enclosure no. 1 assembly
H-1-91600-2	Apatite injection system control enclosure no. 1 wiring diagram
H-1-91600-3	Apatite injection system control enclosure no. 1 wiring diagram
H-1-91601 -1	Apatite injection system control enclosure no. 2 assembly
H-1-91601 -2	Apatite injection system control enclosure no. 2 wiring diagram
H-1-91601 -3	Apatite injection system control enclosure no. 2 wiring diagram

Drawing Number/Sheet	Description
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P&ID = process and instrument diagram

B5 References

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Appendix C

Injected Volumes and Monitored Pressures

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Figures

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This appendix presents the hourly flow rate readings, skid totalizer data, and well totalizer data that were recorded on the skid monitoring data sheet from the apatite injection technical procedure and on the skid monitoring data sheet from the field test instruction (SGW-47614). Both sets of data sheets are included on the accompanying CD (Supporting Information C1: Skid Monitoring Data Sheets from the Apatite Injection Technical Procedure, and Supporting Information C2: Skid Mounting Data Sheets from the Field Test Instruction). The hourly recordings of the injection well pressures are also included on the accompanying CD as Supporting Information C3: Injection Well Pressure Data).

The total volume of apatite-forming solution injected into each well, based on the data recorded on the skid monitoring data sheets, is summarized in Table C-1 for deep upriver wells, Table C-2 for shallow upriver wells, Table C-3 for deep downriver wells, and Table C-4 for shallow downriver wells.

The volume of river water, calcium-citrate, and phosphate injected into each well is summarized in Table C-5 for deep upriver wells, Table C-6 for shallow upriver wells, Table C-7 for deep downriver wells, and Table C-8 for shallow downriver wells. These volumes are calculated using the average percent of river water, calcium-citrate, and phosphate in the blended solution injected by each skid, based on the hourly flow rate readings for that skid, multiplied by the well totalizer volume of solution injected into each well.

The masses of calcium, citrate, and phosphate injected into each well also are summarized in Tables C-5 through C-8. The masses were calculated using two different approaches. The first approach used the volume of calcium citrate injected into each well, multiplied by the chemical makeup concentrations for calcium and citrate, and the volume of phosphate injected into each well, multiplied by the chemical makeup concentrations for phosphate (Table 2-5 in the main text of this report). The second approach used the total volume of calcium citrate, phosphate, and river water injected into each well, multiplied by the average concentrations of calcium, citrate, and phosphate in the three samples of the injection solution collected during the injections. The concentration of calcium was corrected for the calcium present in the river water. The concentration of citrate was calculated based on the concentration of calcium (Appendix F). The wells receiving less than the target phosphate mass are identified with red text in Tables C-5 through C-8.

The total volume of apatite-forming solution injected into each well, based on the well totalizer data recorded on the skid monitoring data sheets, is represented on Figure C-1 for deep upriver wells, Figure C-2 for shallow upriver wells, Figure C-3 for deep downriver wells, and Figure C-4 for shallow downriver wells. The pressure monitoring plots for the wells also are shown on Figures C-1 through C-4. During pressure monitoring for the upriver shallow wells (Figure C-2), the pressure gauges were frequently reported to be "out of service;" out-of-service periods appear as data gaps on the trend plots.

Table C-1. Volumes of High Concentration Solution Injected at Deep Upriver Wells: September 7-9, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Skid 1				
River Water (FQI-N1-1A or 1B)	1,311,079	(346,388)	1,262,392	(333,525)
Calcium-Citrate (FQI-N1-2A or 2B)	127,513	(33,689)	123,425	(32,609)

Table C-1. Volumes of High Concentration Solution Injected at Deep Upriver Wells: September 7-9, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Phosphate (FQI-N1-3A or 3B)	83,577	(22,081)	126,328	(33,376)
Total Solution (FQI-N1-4A or 4B)	End Reading Not Recorded		1,512,123	(399,504)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	1,522,168	(402,158)	1,512,145	(399,510)
199-N-213 (FQI-N1-4)	190,267	(50,269)	Not Applicable	
199-N-217 (FQI-N1-5)	69,019	(18,235)	Not Applicable	
199-N-221 (FQI-N1-6)	178,322	(47,113)	Not Applicable	
199-N-225 (FQI-N1-7)	327,443	(86,511)	Not Applicable	
199-N-229 (FQI-N1-8)	567,078	(149,822)	Not Applicable	
199-N-233 (FQI-N1-9)	145,336	(38,398)	Not Applicable	
Total (Sum of Well Totalizers)	1,477,463	(390,347)	Not Applicable	
Skid 2				
River Water (FQI-N2-1A or 1B)	1,428,016	(377,283)	1,533,758	(405,220)
Calcium-Citrate (FQI-N2-2A or 2B)	64,633	(17,076)	155,155	(40,992)
Phosphate (FQI-N2-3A or 3B)	146,824	(38,791)	157,210	(41,535)
Total Solution (FQI-N2-4A)	Readings Not Recorded		1,719,177	(454,208)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	1,639,473	(433,150)	1,846,122	(487,747)
199-N-211 (FQI-N2-4)	94,614	(24,997)	Not Applicable	
199-N-215 (FQI-N2-5)	49,693	(13,129)	Not Applicable	
199-N-219 (FQI-N2-6)	245,207	(64,784)	Not Applicable	
199-N-223 (FQI-N2-7)	445,078	(117,590)	Not Applicable	
199-N-227 (FQI-N2-8)	368,538	(97,368)	Not Applicable	
199-N-231 (FQI-N2-9)	122,721	(32,423)	Not Applicable	
Total (Sum of Well Totalizers)	1,325,851	(350,291)	Not Applicable	

Table C-2. Volumes of High Concentration Solution Injected at Shallow Upriver Wells: September 13-15, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Skid 1				
River Water (FQI-N1-1A or 1B)	363,905	(96,144)	1,188,679	(314,050)
Calcium-Citrate (FQI-N1-2A or 2B)	117,944	(31,161)	119,027	(31,447)
Phosphate (FQI-N1-3A or 3B)	120,647	(31,875)	119,432	(31,554)
Total Solution (FQI-N1-4A or 4B)	Readings Not Recorded		1,424,012	(376,225)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	602,496	(159,180)	1,427,138	(377,051)
199-N-214 (FQI-N1-4)	213,633	(56,442)	Not Applicable	
199-N-218 (FQI-N1-5)	140,495	(37,119) ^a	Not Applicable	
199-N-222 (FQI-N1-6)	187,380	(49,506)	Not Applicable	
199-N-226 (FQI-N1-7)	320,412	(84,653)	Not Applicable	
199-N-230 (FQI-N1-8)	90,427	(23,891)	Not Applicable	
199-N-234 (FQI-N1-9)	200,264	(52,910)	Not Applicable	
199-N-235 (FQI-N1-8) ^b	28,751	(7,596)	Not Applicable	
Total (Sum of Well Totalizers)	1,181,363	(312,117)	Not Applicable	
Skid 2				
River Water (FQI-N2-1A or 1B)	1,167,252	(308,389)	1,115,913	(294,825)
Calcium-Citrate (FQI-N2-2A or 2B)	114,523	(30,257)	113,217	(29,912)
Phosphate (FQI-N2-3A or 3B)	81,722	(21,591)	113,633	(30,022)
Total Solution (FQI-N2-4A)	Readings Not Recorded		1,342,309	(354,639)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	1,363,497	(360,237)	1,342,763	(354,759)
199-N-212 (FQI-N2-4)	312,834	82,651	Not Applicable	
199-N-216 (FQI-N2-5)	43,153	11,401	Not Applicable	
199-N-220 (FQI-N2-6)	112,744	29,787	Not Applicable	
199-N-224 (FQI-N2-7)	93,054	(24,585) ^c	Not Applicable	
199-N-228 (FQI-N2-8)	347,898	91,915	Not Applicable	
199-N-232 (FQI-N2-9)	338,069	89,318	Not Applicable	

Table C-2. Volumes of High Concentration Solution Injected at Shallow Upriver Wells: September 13-15, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
199-N-238 (FQI-N2-5) ^b	38,191	(10,090)	Not Applicable	
199-N-237 (FQI-N2-6) ^b	24,020	(6,346)	Not Applicable	
199-N-236 (FQI-N2-7) ^b	32,801	(8,666) ^c	Not Applicable	
Total (Sum of Well Totalizers)	1,342,763	(354,759)	Not Applicable	

a. The final totalizer reading was less than the beginning reading. The beginning reading on this totalizer on 9/21/11 was 55,742 gallons. Subtracted 369 gallons (the average difference in the other well totalizer readings between 9/15 and 9/21 on Skid 1) from 55,742 gallons, and subtracted the totalizer start value on 9/13.

b. This downriver well was used for injection for two or three hours at the end of the upriver injection phase.

c. The totalizer did not totalize on FQI-N2-7 (wells 199-N-224 and 199-N-236). The hourly flowrate total minus the sum of the well totalizers is 33,251 gallons. It was assumed that well 199-N-236 received 86 percent of the volume that well 199-N-238 received, based on the ratio of the injected volumes in these two wells during the deep downriver injections. The remaining volume was assumed to be injected at well 199-N-224.

Table C-3. Volumes of High Concentration Solution Injected at Deep Downriver Wells: September 21-23, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Skid 1				
River Water (FQI-N1-1A or 1B)	1,991,474	(526,149)	1,169,111	(308,880)
Calcium-Citrate (FQI-N1-2A or 2B)	156,184	(41,264)	114,390	(30,222)
Phosphate (FQI-N1-3A or 3B)	16,018	(4,232)	116,377	(30,747)
Total Solution (FQI-N1-4A or 4B)	Readings Not Recorded		1,404,375	(371,037)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	2,163,676	(571,645)	1,399,878	(369,849)
199-N-258 (FQI-N1-4)	111,086	(29,349)	Not Applicable	
199-N-254 (FQI-N1-5)	188,940	(49,918)	Not Applicable	
199-N-250 (FQI-N1-6)	256,661	(67,810)	Not Applicable	
199-N-246 (FQI-N1-7)	264,818	(69,965)	Not Applicable	
199-N-242 (FQI-N1-8)	51,764	(13,676)	Not Applicable	
199-N-238 (FQI-N1-9)	351,309	(92,816)	Not Applicable	
Total (Sum of Well Totalizers)	1,224,576	(323,534)	Not Applicable	

Table C-3. Volumes of High Concentration Solution Injected at Deep Downriver Wells: September 21-23, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Skid 2				
River Water (FQI-N2-1A or 1B)		(-671,737)	1,249,504	(330,120)
Calcium-Citrate (FQI-N2-2A or 2B)		(-35,511)	123,724	(32,688)
Phosphate (FQI-N2-3A or 3B)	1,169,111	(42,337)	126,165	(33,333)
Total Solution (FQI-N2-4A)	Readings Not Recorded		1,499,394	(396,141)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)		(-664,911)	1,499,394	(396,141)
199-N-256 (FQI-N2-4)	192,445	(50,844)	Not applicable	
199-N-252 (FQI-N2-5)	219,167	(57,904)	Not applicable	
199-N-248 (FQI-N2-6)	236,036	(62,361)	Not applicable	
199-N-244 (FQI-N2-7)	58,565	(15,473)	Not applicable	
199-N-240 (FQI-N2-8)	85,583	(22,611)	Not applicable	
199-N-236 (FQI-N2-9)	301,744	(79,721)	Not applicable	
Total (Sum of Well Totalizers)	1,093,539	(288,914)	Not applicable	

Table C-4. Volumes of High Concentration Solution Injected at Shallow Downriver Wells: September 23-25, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
Skid 1				
River Water (FQI-N1-1A or 1B)	251,271	(66,386)	1,078,271	(284,880)
Calcium-Citrate (FQI-N1-2A or 2B)	6,998	(1,849)	106,271	(28,077)
Phosphate (FQI-N1-3A or 3B)	182,573	(48,236)	104,988	(27,738)
Total Solution (FQI-N1-4A or 4B)	Readings Not Recorded		1,289,531	(340,695)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	440,843	(116,471)	1,289,531	(340,695)
199-N-237 (FQI-N1-4)	77,994	(20,606)	Not applicable	
199-N-241 (FQI-N1-5)	111,249	(29,392)	Not applicable	

Table C-4. Volumes of High Concentration Solution Injected at Shallow Downriver Wells: September 23-25, 2011

Location	Volume Injected Based on Flow Totalizer Readings		Volume Injected Based on Hourly Flow Rate Recordings	
	Liters	(Gallons)	Liters	(Gallons)
199-N-245 (FQI-N1-6)	246,067	(65,011)	Not applicable	
199-N-249 (FQI-N1-7)	230,370	(60,864)	Not applicable	
199-N-253 (FQI-N1-8)	153,629	(40,589)	Not applicable	
199-N-257 (FQI-N1-9)	509,192	(134,529)	Not applicable	
Total (Sum of Well Totalizers)	1,328,501	(350,991)	Not applicable	
Skid 2				
River Water (FQI-N2-1A or 1B)	610,127	(161,196)	1,005,599	(265,680)
Calcium-Citrate (FQI-N2-2A or 2B)	324,867	(85,830)	100,549	(26,565)
Phosphate (FQI-N2-3A or 3B)		(-2,997)	99,720	(26,346)
Total Solution (FQI-N2-4A)	Readings Not Recorded		1,205,890	(318,597)
Total (Sum of River Water, Calcium-Citrate, and Phosphate)	923,650	(244,029)	1,205,867	(318,591)
199-N-235 (FQI-N2-4)	188,822	(49,887)	Not applicable	
199-N-239 (FQI-N2-5)	4,508	(1,191)	Not applicable	
199-N-243 (FQI-N2-6)	86,756	(22,921)	Not applicable	
199-N-247 (FQI-N2-7)	22,589	(5,968)	Not applicable	
199-N-251 (FQI-N2-8)	435,994	(115,190)	Not applicable	
199-N-255 (FQI-N2-9)	95	(25)	Not applicable	
Total (Sum of Well Totalizers)	738,764	(195,182)	Not applicable	

Table C-5. Volume and Mass of Chemicals Injected in Deep Upriver Wells: September 7-9, 2011

	Volume Injected (Liters [Gallons]) Based on Hourly Data ^a			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^d	Calculated Period of Performance (Years)
	River Water	Calcium-Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^c		
Skid 1											
199-N-213	158,841 (41,966)	15,530 (4,103)	15,897 (4,200)	27	318	726	28	335	731	1.625	519
199-N-217	57,619 (15,223)	5,632 (1,488)	57,65 (1,523)	10	115	263	10	122	265	0.589	189
199-N-221	148,868 (39,331)	14,553 (3,845)	14,898 (3,936)	25	298	681	27	314	685	1.523	486
199-N-225	273,360 (72,222)	26,726 (7,061)	27,354 (7,227)	47	547	1250	49	577	1258	2.796	893
199-N-229	473,416 (125,077)	46,287 (12,229)	47,377 (12,517)	81	947	2164	85	999	2179	4.842	1546
199-N-233	121,332 (32,056)	11,862 (3,134)	12,142 (3,208)	21	243	555	22	256	559	1.241	397
Skid 2											
199-N-211	78,603 (20,767)	7,952 (2,101)	8,058 (2,129)	14	163	368	13	159	360	0.799	255

Table C-5. Volume and Mass of Chemicals Injected in Deep Upriver Wells: September 7-9, 2011

	Volume Injected (Liters [Gallons]) Based on Hourly Data ^a			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^d	Calculated Period of Performance (Years)
	River Water	Calcium Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^c		
199-N-215	41,287 (10,908)	4,175 (1,103)	4,232 (1,118)	7	85	193	7	83	189	0.420	134
199-N-219	203,720 (53,823)	20,609 (5,445)	20,882 (5,517)	36	422	954	35	411	932	2.070	661
199-N-223	369,772 (97,694)	37,407 (9,883)	37,903 (10,014)	65	765	1731	63	746	1691	3.758	1200
199-N-227	306,180 (80,893)	30,973 (8,183)	31,385 (8,292)	54	634	1434	52	618	1400	3.111	993
199-N-231	101,957 (26,937)	10,314 (2,725)	10,450 (2,761)	18	211	477	17	206	466	1.036	331

a. Based on the hourly readings on Skid 1 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 1 wells averaged 83.48 percent river water, 8.16 percent calcium citrate, and 8.35 percent phosphate. Based on the hourly readings on Skid 2 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 2 wells averaged 83.08 percent river water, 8.40 percent calcium citrate, and 8.52 percent phosphate. These percentages were multiplied by the totalizer volumes injected into each well to obtain the values in this table.

b. Calcium concentrations in samples corrected for contribution by river water. Phosphate concentrations in samples not corrected for contribution by river water.

c. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg (Appendix F). Wells receiving less than the target phosphate mass are identified with red text.

d. Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment.

Table C-6. Volume and Mass of Chemicals Injected in Shallow Upriver Wells: September 13-15, 2011

	Volume Injected (Gallons) Based on Hourly Data ^a			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^d	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^c		
Skid 1											
199-N-214	177,937 (47,011)	17,816 (4,707)	17,877 (4,723)	31	364	817	29	346	823	1.829	584
199-N-218	117,021) (30,917)	11,718 (3,096)	11,756 (3,106)	20	240	537	19	228	541	1.203	384
199-N-222	156,071 (41,234)	15,268 (4,129)	15,681 (4,143)	27	320	716	26	304	722	1.604	512
199-N-226	266,877 (70,509)	26,722 (7,060)	26,813 (7,084)	47	547	1225	44	519	1235	2.743	876
199-N-230	75,318 (19,899)	7,544 (1,993)	7,566 (1,999)	13	154	346	12	146	348	0.774	248
199-N-234	166,801 (44,069)	16,703 (4,413)	16,760 (4,428)	29	342	766	28	324	772	1.715	548
Skid 2											
199-N-212	259,984 (68,688)	26,378 (6,969)	26,472 (6,994)	46	540	1209	44	524	1215	2.699	862

Table C-6. Volume and Mass of Chemicals Injected in Shallow Upriver Wells: September 13-15, 2011

	Volume Injected (Gallons) Based on Hourly Data ^a			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^d	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^c		
199-N-216	35,863 (9,475)	3,637 (961)	3,653 (965)	6	74	167	6	72	168	0.372	119
199-N-220	93,698 (24,755)	9,508 (2,512)	9,542 (2,521)	17	194	436	16	189	438	0.973	311
199-N-224	77,335 (20,432)	7,846 (2,073)	7,877 (2,081)	14	160	360	13	156	361	0.803	257
199-N-228	289,125 (76,387)	29,334 (7,750)	29,440 (7,778)	51	600	1345	49	583	1351	3.002	958
199-N-232	280,953 (74,228)	28,505 (7,531)	28,611 (7,559)	50	583	1307	48	566	1313	2.917	931

a. Based on the hourly readings on Skid 1 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 1 wells averaged 83.29 percent river water, 8.34 percent calcium citrate, and 8.37 percent phosphate. Based on the hourly readings on Skid 2 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 2 wells averaged 83.11 percent river water, 8.43 percent calcium citrate, and 8.46 percent phosphate. These percentages were multiplied by the totalizer volumes injected into each well to obtain the values in this table.

b. Calcium concentrations in samples corrected for contribution by river water. Phosphate concentrations in samples not corrected for contribution by river water.

c. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg (Appendix F). Wells receiving less than the target phosphate mass are identified with red text.

d. Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment.

Table C-7. Volume and Mass of Chemicals Injected in Deep Downriver Wells: September 21-23, 2011

	Volume Injected (Gallons) Based on Hourly Data ^{a,c}			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^e	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^d		
Skid 1											
199-N-258	92,774 (24,511)	9,076 (2,398)	9,235 (2,440)	16	186	422	16	187	427	0.949	303
199-N-254	157,793 (41,689)	15,439 (4,079)	15,708 (4,150)	27	316	718	27	318	726	1.613	515
199-N-250	214,352 (56,632)	20,973 (5,541)	21,336 (5,637)	37	429	975	37	431	986	2.192	700
199-N-246	221,161 (58,431)	21,639 (5,717)	22,014 (5,816)	38	443	1006	38	445	1018	2.261	722
199-N-242	43,232 (11,422)	4,232 (1,118)	4,304 (1,137)	7	87	197	7	87	199	0.442	142
199-N-238	325,135 (85,901)	31,926 (8,435)	32,437 (8,570)	56	653	1482	56	654	1499	3.326	1062
Skid 2											
199-N-256	160,370 (42,370)	15,878 (4,195)	16,192 (4,278)	28	325	740	27	320	743	1.652	528

Table C-7. Volume and Mass of Chemicals Injected in Deep Downriver Wells: September 21-23, 2011

	Volume Injected (Gallons) Based on Hourly Data ^{a,c}			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^e	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^d		
199-N-252	182,641 (48,254)	18,085 (4,778)	18,441 (4,872)	32	370	842	31	365	847	1.881	601
199-N-248	196,699 (51,968)	19,478 (5,146)	19,860 (5,247)	34	398	907	33	393	912	2.026	647
199-N-244	48,804 (12,894)	4,833 (1,277)	4,928 (1,302)	8	99	225	8	97	226	0.503	161
199-N-240	71,321 (18,843)	7,063 (1,866)	7,203 (1,903)	12	144	329	12	142	331	0.735	235
199-N-236	278,716 (73,637)	27,665 (7,309)	28,164 (7,441)	48	566	1287	47	557	1293	2.872	917

a. Based on the hourly readings on Skid 1 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 1 wells averaged 83.52 percent river water, 8.17 percent calcium citrate, and 8.31 percent phosphate. Based on the hourly readings on Skid 2 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 2 wells averaged 83.33 percent river water, 8.25 percent calcium citrate, and 8.41 percent phosphate. These percentages were multiplied by the totalizer volumes injected into each well to obtain the values in this table.

b. Calcium concentrations in samples corrected for contribution by river water. Phosphate concentrations in samples not corrected for contribution by river water.

c. Wells 199-N-236 and 199-N-238 were injected for 3 hours during upriver injections. The values for these wells in this table include the upriver injection data.

d. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg (Appendix F). Wells receiving less than the target phosphate mass are identified with red text.

e. Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment.

Table C-8. Volume and Mass of Chemicals Injected in Shallow Downriver Wells: September 23-25, 2011

	Volume Injected (Gallons) Based on Hourly Data ^{a,c}			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^e	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^d		
Skid 1											
199-N-237	85,178 (22,504)	8,452 (2,233)	8,384 (2,215)	15	173	383	15	172	379	0.830	265
199-N-241	93,024 (24,577)	9,167 (2,422)	9,058 (2,393)	16	188	414	16	188	407	0.905	289
199-N-245	205,753 (54,360)	20,280 (5,358)	20,034 (5,293)	35	415	915	35	415	901	2.001	639
199-N-249	192,630 (50,893)	18,986 (5,016)	18,755 (4,955)	33	388	857	33	388	843	1.873	598
199-N-253	128,459 (33,939)	12,661 (3,345)	12,509 (3,305)	22	259	571	22	259	562	1.249	399
199-N-257	425,775 (112,490)	44,689 (11,807)	41,457 (10,953)	73	858	1894	73	859	1864	4.141	1322
Skid 2											
199-N-235	181,411 (47,929)	18,142 (4,793)	18,020 (4,761)	32	371	823	31	365	815	1.803	576

Table C-8. Volume and Mass of Chemicals Injected in Shallow Downriver Wells: September 23-25, 2011

	Volume Injected (Gallons) Based on Hourly Data ^{a,c}			Mass Injected (kg) Based on Solution Volume and Chemical Makeup Concentration (Table 2-5)			Mass Injected (kg) Based on Mixture Volume and Skid Sample Average Concentration (Table 3-5) ^b			Apatite Concentration (mg Apatite/g Sediment) ^e	Calculated Period of Performance (Years)
	River Water	Calcium -Citrate	Phosphate	Calcium	Citrate	Phosphate	Calcium	Citrate	Phosphate ^d		
199-N-239	3,759 (993)	375 (99)	371 (98)	1	8	17	1	8	17	0.037	12
199-N-243	72,346 (19,114)	7,233 (1,911)	7,173 (1,895)	13	148	328	12	146	324	0.719	230
199-N-247	18,838 (4,977)	1,885 (498)	1,870 (494)	3	39	85	3	38	84	0.187	60
199-N-251	363,583 (96,059)	36,355 (9,605)	36,056 (9,526)	63	744	1647	62	735	1626	3.613	1154
199-N-255	79 (21)	8 (2)	8 (2)	0	0	0	0	0	0	0.001	1

a. Based on the hourly readings on Skid 1 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 1 wells averaged 83.62 percent river water, 8.24 percent calcium citrate, and 8.14 percent phosphate. Based on the hourly readings on Skid 2 for the river water, calcium citrate solution, and phosphate solution, the mixed solution injected into the Skid 2 wells averaged 83.39 percent river water, 8.34 percent calcium citrate, and 8.27 percent phosphate. These percentages were multiplied by the totalizer volumes injected into each well to obtain the values in this table.

b. Calcium concentrations in samples corrected for contribution by river water. Phosphate concentrations in samples not corrected for contribution by river water.

c. Well 199-N-235 was injected for 2 hours and well 199-N-237 was injected for 3 hours during upriver injections. The values for these wells in this table include the upriver injection data.

d. The mass of phosphate per well needed to meet the 0.544 mg phosphate/g sediment target is 432 kg (Appendix F). Wells receiving less than the target phosphate mass are identified with red text.

e. Based on the 0.544 mg phosphate/g sediment target, the target apatite concentration per well is 0.96 mg apatite/g sediment.

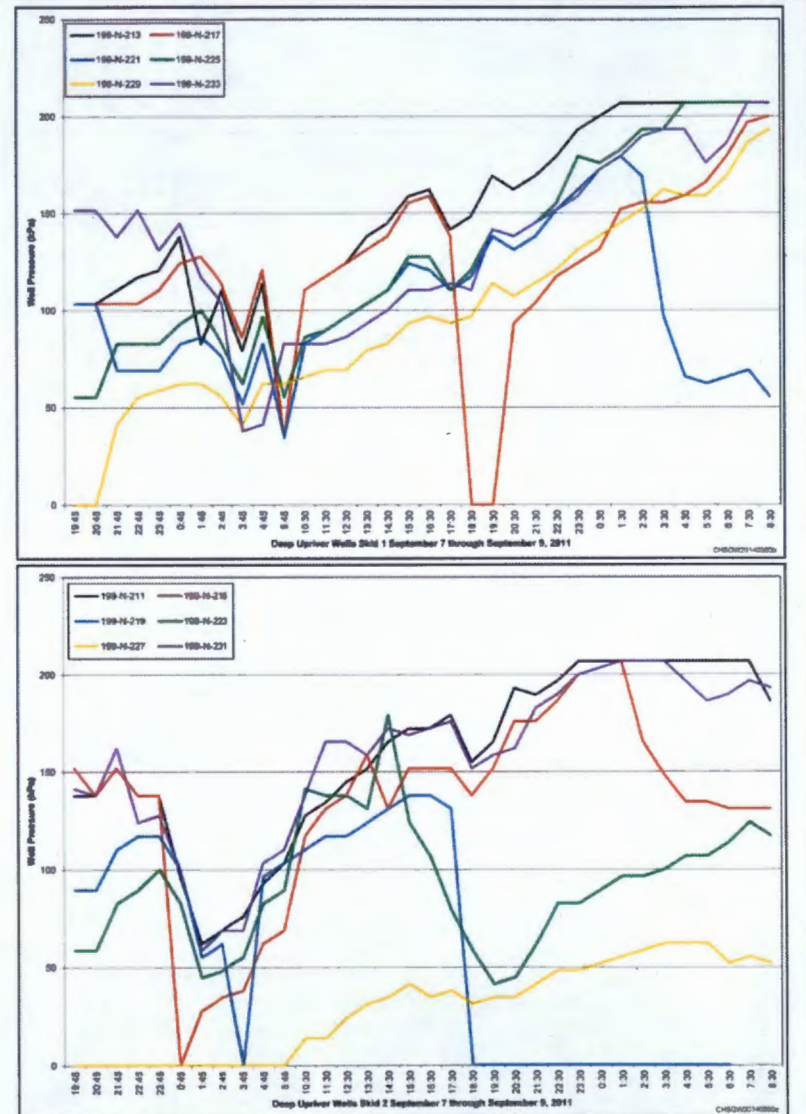
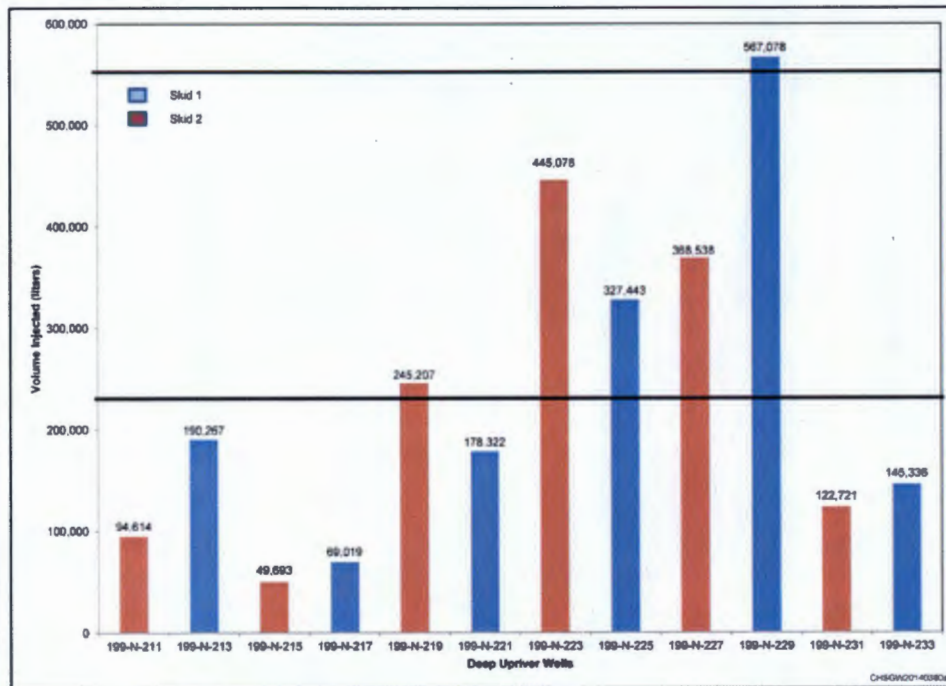


Figure C-1. Well Volumes and Pressures for Deep Upriver Wells

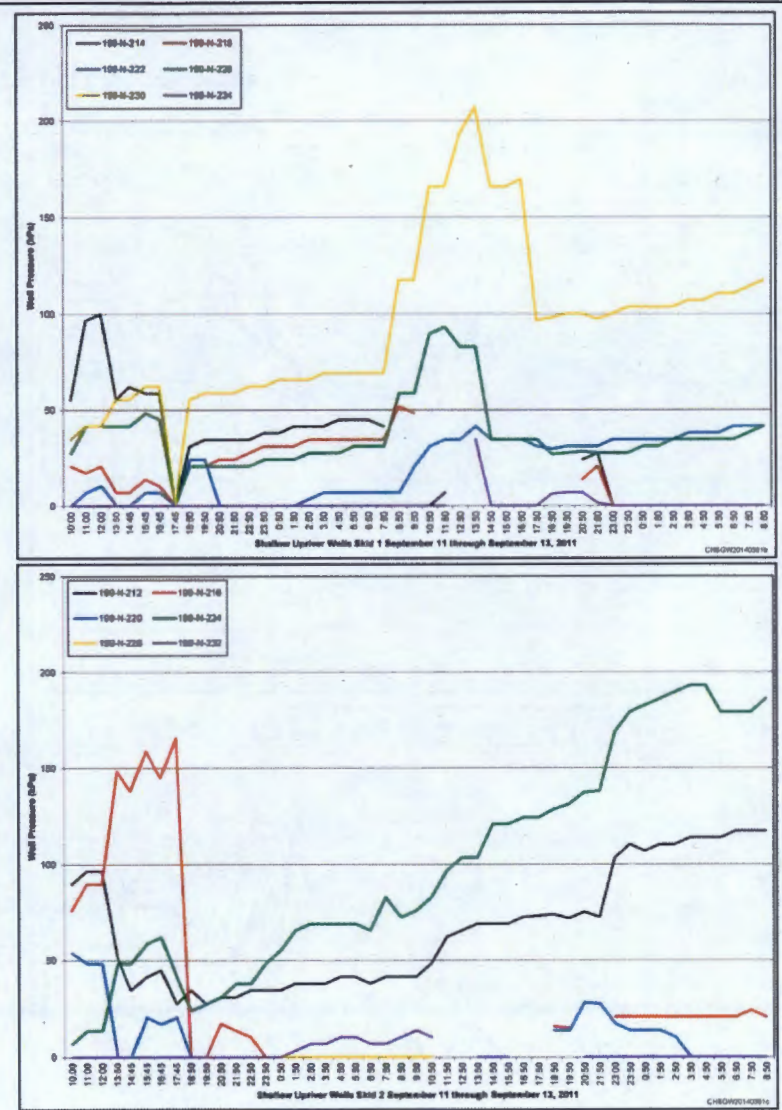
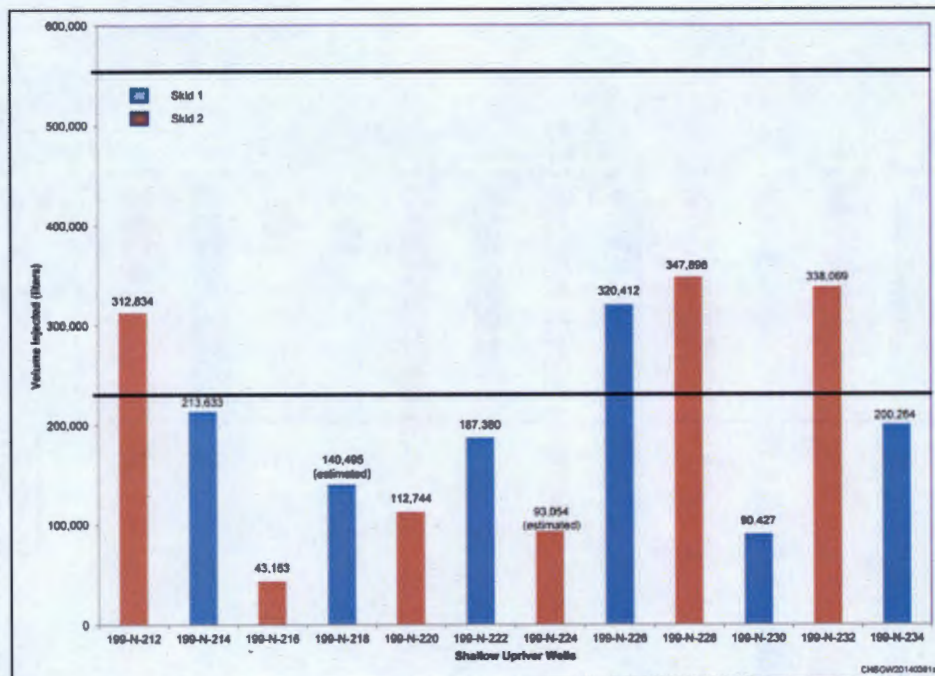


Figure C-2. Well Volumes and Pressures for Shallow Upriver Wells

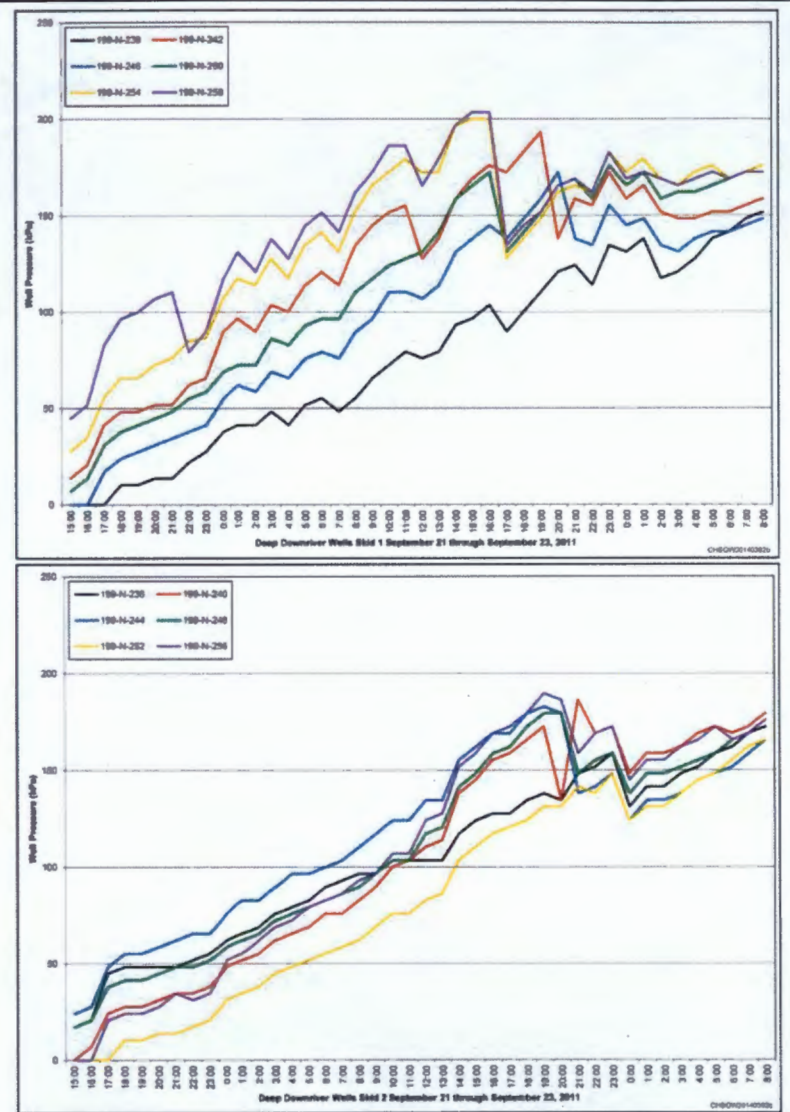
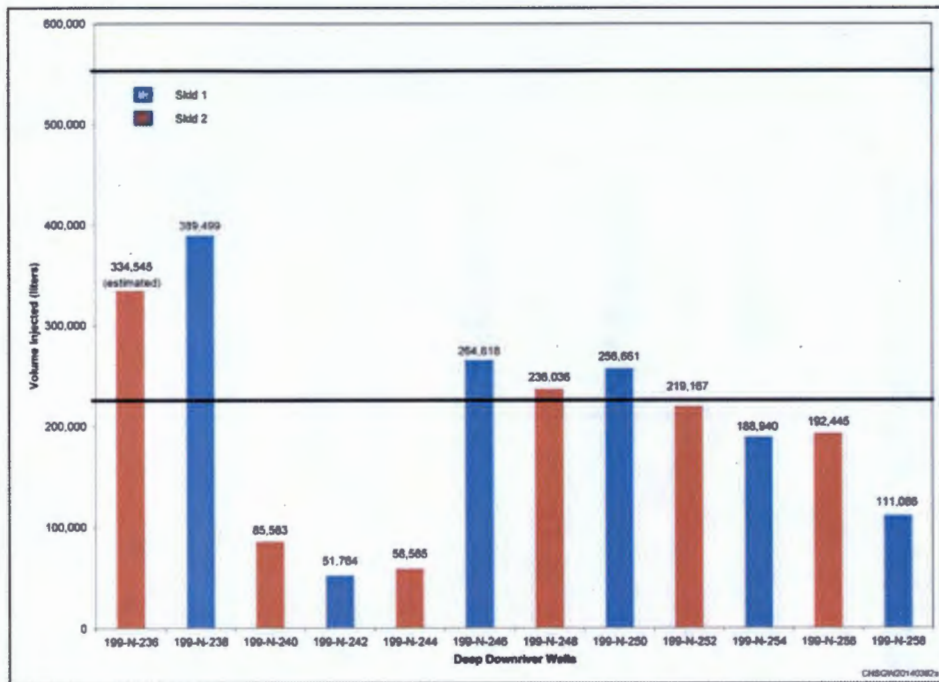


Figure C-3. Well Volumes and Pressures for Deep Downriver Wells

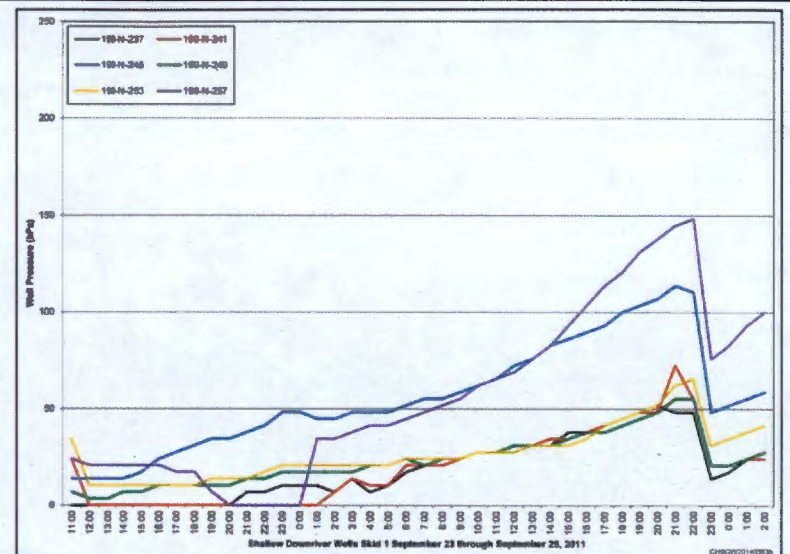
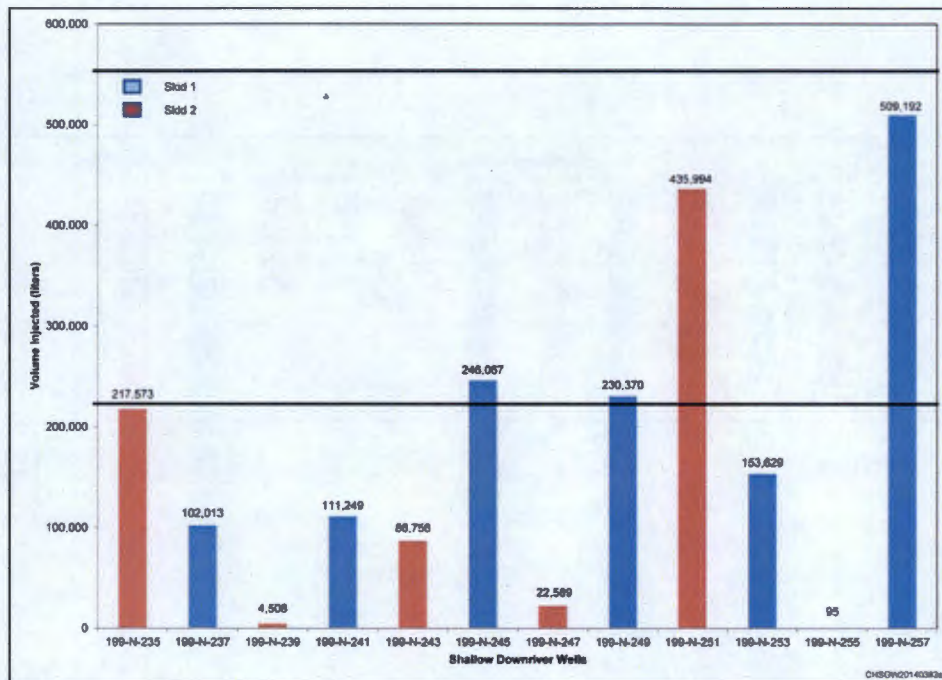


Figure C-4. Well Volumes and Pressures for Shallow Downriver Wells

Appendix D
Injection Skid Analytical Data

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This appendix provides all of the analytical and field results for samples of river water and injection chemicals collected during the injections in 2011. The results for calcium and phosphate are summarized in Table D-1.

All of the data presented in this appendix are provided as an electronic file on the accompanying CD as Supporting Information D-1.

The data are stored in the Hanford Environmental Information System database, and users also may retrieve the data via the internet through the DOE Environmental Dashboard Application available at: <http://environet.hanford.gov/EDA/>.

Table D-1. Concentrations of Calcium, Citrate, and Phosphate in Injection Mixtures Sampled at the Skids

Sample Location	Sample Date ^a	Sample Time ^a	Calcium (µg/L)	Citrate (µg/L) ^b	Phosphate (µg/L)
Skid 1 Deep Upriver Wells					
Columbia River Water	09/07/2011	17:20	17,900	Assumed to be 0	307 UD
First Skid Sample	09/07/2011	17:20	172,000	1,762	3,960,000
Second Skid Sample	09/08/2011	12:20	168,000		3,860,000
Third Skid Sample	09/09/2011	7:30	149,000		3,710,000
Skid 2 Deep Upriver Wells					
Columbia River Water	09/07/2011	13:30	17400	Assumed to be 0	307 UD
First Skid Sample	09/07/2011	13:30	158,000	1,677	3,800,000
Second Skid Sample	09/08/2011	12:00	161,000		3,830,000
Third Skid Sample	09/09/2011	7:30	151,000		3,770,000
Skid 1 Shallow Upriver Wells					
Columbia River Water	09/13/2011	9:20	17,100	Assumed to be 0	307 UD
First Skid Sample	09/13/2011	9:50	148,000	1,620	3,990,000
Second Skid Sample	09/14/2011	10:50	155,000		3,830,000
Third Skid Sample	09/15/2011	13:25	152,000		3,740,000
Skid 2 Shallow Upriver Wells					
Columbia River Water	09/13/2011	9:25	17,200	Assumed to be 0	307 UD
First Skid Sample	09/13/2011	9:50	162,000	1,674	3,960,000
Second Skid Sample	09/14/2011	9:50	151,000		3,800,000
Third Skid Sample	09/15/2011	13:25	156,000		3,890,000
Skid 1 Deep Downriver Wells					
Columbia River Water	09/21/2011	13:30	16,900	Assumed to be 0	307 UD

Table D-1. Concentrations of Calcium, Citrate, and Phosphate in Injection Mixtures Sampled at the Skids

Sample Location	Sample Date ^a	Sample Time ^a	Calcium (µg/L)	Citrate (µg/L) ^b	Phosphate (µg/L)
First Skid Sample	09/21/2011	15:00	156,000	1,681	3,800,000
Second Skid Sample	09/22/2011	14:00	162,000		3,770,000
Third Skid Sample	09/23/2011	10:56	152,000		3,960,000
Skid 2 Deep Downriver Wells					
Columbia River Water	09/21/2011	14:00	17,000	Assumed to be 0	307 UD
First Skid Sample	09/21/2011	15:00	154,000	1,664	3,770,000
Second Skid Sample	09/22/2011	14:00	159,000		3,830,000
Third Skid Sample	09/23/2011	10:56	153,000		3,990,000
Skid 1 Shallow Downriver Wells					
Columbia River Water	09/23/2011	11:12	17,100	Assumed to be 0	3,070 UD
First Skid Sample	09/23/2011	19:00	156,000	1,686	3,770,000
Second Skid Sample	09/24/2011	11:10	157,000		3,710,000
Third Skid Sample	09/25/2011	1:00	159,000		3,500,000
Skid 2 Shallow Downriver Wells					
Columbia River Water	09/23/2011	11:12	16,900	Assumed to be 0	3,070 UD
First Skid Sample	09/23/2011	19:00	154,000	1,685	3,800,000
Second Skid Sample	09/24/2011	11:00	157,000		3,800,000
Third Skid Sample	09/25/2011	1:00	160,000		3,590,000

a. Based on HEIS F06-027.

b. Calculated using the calcium concentration in the skid samples (corrected for the river contribution) and based on the mixture formulation, in which the citrate concentration is 2.5 times the calcium concentration.

U = undetected

D = analyte was identified in an analysis at a secondary dilution factor (i.e., dilution factor different than 1.0).

Appendix E

Water Level Elevations During 2011 Injections

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This appendix summarizes the water level elevations during the 2011 apatite barrier well injections. The water levels are based on automated water level monitoring at Well 199-N-146. The average, maximum, and minimum water level elevations for the injection period and for the injection period plus the seven day reaction period are presented in Table E-1 for each phase of injections. Table E-1 also lists the elevation of the top and bottom of the screened interval for each injection well.

Table E-1. Water Level Elevations during 2011 Apatite Barrier Well Injections Based on 199-N-146 Automated Water Level Monitoring

Well Name/Identification	Screened Interval Elevation (m)		Injection Start	Injection Stop	Injection Period Water Level Elevation (m)			Injection + 7 Day Reaction Period Water Level Elevation (m)		
	Top	Bottom			Average	Maximum	Minimum	Average	Maximum	Minimum
Upriver of Original Barrier										
199-N-211/C7316 (Deep)	118.3	116.1	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-212/C7315 (Shallow)	120.5	119.0	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-213/C7314 (Deep)	118.2	116.1	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8
199-N-214/C7313 (Shallow)	120.5	119.0	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-215/C7312 (Deep)	118.1	116.0	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-216/C7311 (Shallow)	120.4	118.9	09/13/2011 09:25	09/15/2011 11:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-217/C7310 (Deep)	117.8	115.7	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8
199-N-218/C7309 (Shallow)	120.1	118.6	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-219/C7308 (Deep)	117.7	115.6	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-220/C7307 (Shallow)	120.2	118.7	09/13/2011 09:25	09/15/2011 11:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-221/C7306 (Deep)	117.7	115.6	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8

Table E-1. Water Level Elevations during 2011 Apatite Barrier Well Injections Based on 199-N-146 Automated Water Level Monitoring

Well Name/Identification	Screened Interval Elevation (m)		Injection Start	Injection Stop	Injection Period Water Level Elevation (m)			Injection + 7 Day Reaction Period Water Level Elevation (m)		
	Top	Bottom			Average	Maximum	Minimum	Average	Maximum	Minimum
199-N-222/C7305 (Shallow)	120.2	118.7	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-223/C7304 (Deep)	117.8	115.6	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-224/C7303 (Shallow)	120.2	118.7	09/13/2011 09:25	09/15/2011 11:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-225/C7302 (Deep)	118.1	116.0	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8
199-N-226/C7301 (Shallow)	120.5	118.9	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-227/C7300 (Deep)	117.9	115.7	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-228/C7299 (Shallow)	120.4	118.9	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-229/C7298 (Deep)	117.9	115.7	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8
199-N-230/C7297 (Shallow)	120.1	118.6	09/13/2011 09:25	09/15/2011 12:25	118.2	118.4	117.8	118.0	118.4	117.5
199-N-231/C7296 (Deep)	117.7	115.6	09/07/2011 13:30	09/09/2011 13:00	118.4	118.6	118.2	118.2	118.6	117.8
199-N-232/C7295 (Shallow)	120.3	118.7	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5

Table E-1. Water Level Elevations during 2011 Apatite Barrier Well Injections Based on 199-N-146 Automated Water Level Monitoring

Well Name/Identification	Screened Interval Elevation (m)		Injection Start	Injection Stop	Injection Period Water Level Elevation (m)			Injection + 7 Day Reaction Period Water Level Elevation (m)		
	Top	Bottom			Average	Maximum	Minimum	Average	Maximum	Minimum
199-N-233/C7294 (Deep)	117.8	115.6	09/07/2011 17:20	09/09/2011 13:00	118.5	118.6	118.3	118.2	118.6	117.8
199-N-234/C7293 (Shallow)	120.3	118.8	09/13/2011 09:25	09/15/2011 14:25	118.2	118.4	117.8	118.0	118.4	117.5
Downriver of Original Barrier										
199-N-235/C7328 (Shallow) ^a	119.0	117.5	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-236/C7329 (Deep) ^b	116.7	114.6	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-237/C7330 (Shallow) ^b	119.1	117.6	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-238/C7331 (Deep) ^b	116.7	114.6	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-239/C7332 (Shallow)	119.1	117.6	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-240/C7333 (Deep)	117.0	114.9	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-241/C7334 (Shallow)	119.3	117.8	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-242/C7335 (Deep)	116.8	114.7	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-243/C7336 (Shallow)	119.2	117.7	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6

Table E-1. Water Level Elevations during 2011 Apatite Barrier Well Injections Based on 199-N-146 Automated Water Level Monitoring

Well Name/Identification	Screened Interval Elevation (m)		Injection Start	Injection Stop	Injection Period Water Level Elevation (m)			Injection + 7 Day Reaction Period Water Level Elevation (m)		
	Top	Bottom			Average	Maximum	Minimum	Average	Maximum	Minimum
199-N-244/C7337 (Deep)	117.2	115.0	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-245/C7338 (Shallow)	119.2	117.7	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-246/C7339 (Deep)	117.0	114.8	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-247/C7340 (Shallow)	119.2	117.7	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-248/C7341 (Deep)	116.9	114.8	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-249/C7342 (Shallow)	119.1	117.6	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-250/C7343 (Deep)	116.7	114.6	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-251/C7344 (Shallow)	119.1	117.5	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-252/C7345 (Deep)	116.8	114.7	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-253/C7346 (Shallow)	119.0	117.5	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-254/C7347 (Deep)	116.7	114.5	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6

Table E-1. Water Level Elevations during 2011 Apatite Barrier Well Injections Based on 199-N-146 Automated Water Level Monitoring

Well Name/Identification	Screened Interval Elevation (m)		Injection Start	Injection Stop	Injection Period Water Level Elevation (m)			Injection + 7 Day Reaction Period Water Level Elevation (m)		
	Top	Bottom			Average	Maximum	Minimum	Average	Maximum	Minimum
199-N-255/C7348 (Shallow)	118.8	117.3	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-256/C7349 (Deep)	116.5	114.4	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6
199-N-257/C7350 (Shallow)	118.8	117.2	09/23/2011 10:30	09/25/2011 02:00	118.1	118.3	117.9	117.9	118.3	117.6
199-N-258/C7351 (Deep)	116.5	114.4	09/21/2011 13:30	09/23/2011 08:00	117.9	118.1	117.7	117.9	118.3	117.6

a. Also injected from 09/15/2011 12:25 to 09/15/2011 14:25.

b. Also injected from 09/15/2011 11:25 to 09/15/2011 14:25.

Appendix F

Injection Calculation Brief ECF-100NR2-14-0040

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The purpose of the calculation brief provided in this appendix is to document and describe the assumptions and methodology used to determine the amount of phosphate emplaced within the saturated sediments of the 100-NR-2 Operable Unit apatite permeable reactive barrier during injections performed in September of 2011.

Calculation brief ECF-100NR2-14-0040, Revision 0, is included on the accompanying CD as Supporting Information F-1.

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Appendix G

Post-Injection Analytical Data for Apatite Permeable Reactive Barrier Performance Monitoring Wells and Aquifer Tubes

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This appendix provides all of the analytical and field results for groundwater samples collected in 2011 from the 100-N apatite permeable reactive barrier performance monitoring wells and aquifer tubes downgradient from the 91 m (300 ft) long upriver and 91 m (300 ft) long downriver segments that were injected in 2011. Three sets of samples were collected within five weeks following completion of the injections. These results are post-injection concentrations.

All of the groundwater data presented in this appendix are provided as an electronic file on the accompanying CD as Supporting Information G-1.

The data are stored in the Hanford Environmental Information System database, and users also may retrieve the data via the internet through the DOE Environmental Dashboard Application available at: <https://ehs.hanford.gov/eda/>.

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Appendix H

Data Validation Report for Analytical Data Collected as Part of the Design Optimization Study

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Data validation was performed for the analytical data collected as part of the design optimization study. Analytical data were available for the samples of river water and injection chemicals collected during the injections (Appendix D of this report) and the samples of groundwater collected following the injections at monitoring wells and aquifer tubes (Appendix G of this report). Data validation was performed in accordance with the design optimization study (Section 8.1 of DOE/RL-2010-29¹), as described in Section 3.4 in the main text of this report.

The data validation report for this appendix is provided as an electronic file on the accompanying CD as Supporting Information H-1.

¹ DOE/RL-2010-29, 2010, *Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: <http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1010051004>.

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